



LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF MERCURY AND MERCURY COMPOUNDS



Locating And Estimating Air Emissions From Sources of Mercury and Mercury Compounds

Office of Air Quality Planning and Standards
Office of Air and Radiation
U.S. Environmental Protection Agency
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EXECUTIVE SUMMARY

The emissions of mercury and mercury compounds into the atmosphere are of special significance because of the Clean Air Act Amendments of 1990 (CAAA). Sections of the CAAA that may require information on mercury emissions include 112(n)(1)(A, B, C), 112(c)(6), 112(m), 112(o)(1), 112(k), and 129. This document is designed to assist groups interested in inventorying air emissions of mercury by providing a compilation of available information on sources and emissions of these substances.

In the U.S., mercury is produced primarily as a byproduct of gold mining and as a result of secondary production (i.e., recycling or mercury recovery from products or by-products); the last mercury mine was closed in 1990. In 1995, the total U.S. supply of mercury was 911 Mg (1,002 tons), of which approximately 41 percent resulted from imports. The demand for mercury in the U.S. has decreased sharply (64 percent) since 1989. In 1995, the U.S. demand was 436 Mg (480 tons) or 48 percent of the supply.

In 1995, seven source categories accounted for the U.S. demand for mercury; the chlor-alkali industry was the major user. Other major users of mercury were for wiring devices and switches and production of measurement and control instruments. These three source categories accounted for about 65 percent of the total U.S. demand for mercury; the other four source categories accounted for the remaining 35 percent.

Nationwide mercury emissions were estimated for several source types for the years 1994/1995. These were the latest years for which adequate information was available for almost all source types. The total nationwide mercury emissions estimate was 140 Mg (154 tons) from five major source types. Table ES-1 shows the estimated nationwide emissions by major source types and the percent contribution of each type to the total emissions. The three specific sources emitting the largest quantities of mercury were coal combustion, municipal waste combustion, and medical waste combustion.

TABLE ES-1. ESTIMATED NATIONWIDE EMISSIONS

Major source type	Estimated nationwide emissions, Mg (tons)	Percent of total emissions
Mercury and mercury compound production	0.13 (0.14)	< 0.1
Major uses of mercury	7.3 (8.0)	5.2
Combustion sources	123.0 (135.6)	88.0
Miscellaneous manufacturing processes	8.1 (8.9)	5.8
Other miscellaneous sources	1.3 (1.5)	0.9
TOTAL	140 (154)	100

1.0 PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the environment that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Typically, however, little information exists on the magnitude of the emissions of these substances or about the sources that may be emitting them to the atmosphere.

To assist groups interested in inventorying air emissions of various hazardous chemicals and metals, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. Prior documents in the series are listed below:

<u>Substance</u>	<u>EPA Publication No.</u>
Acrylonitrile	EPA-450/4-84-007a
Carbon Tetrachloride	EPA-450/4-84-007b
Chloroform	EPA-450/4-84-007c
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde	EPA-450/4-91-012
Nickel	EPA-450/4-84-007f
Chromium	EPA-450/4-84-007g
Manganese	EPA-450/4-84-007h
Phosgene	EPA-450/4-84-007i
Epichlorohydrin	EPA-450/4-84-007j
Vinylidene Chloride	EPA-450/4-84-007k
Ethylene Oxide	EPA-450/4-84-007l
Chlorobenzene	EPA-450/4-84-007m
Polychlorinated Biphenyls (PCB's)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)/ Polycyclic Aromatic Hydrocarbons (PAH)	EPA-450/4-84-007p
Benzene	EPA-450/4-84-007q
Perchloroethylene and Trichloroethylene	EPA-450/2-89-013
Municipal Waste Combustion	EPA-450/2-89-006
Coal and Oil Combustion Sources	EPA-450/2-89-001
1,3-Butadiene	EPA-450/2-89-021
Chromium (Supplement)	EPA-450/2-89-002
Sewage Sludge	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Cadmium and Cadmium Compounds	EPA-454/R-93-040
Cyanide Compounds	EPA-454/R-93-041
Methylene Chloride	EPA-454/R-93-006
Medical Waste Incinerators	EPA-454/R-93-053
TCDD/TCDF	Draft
Toluene	EPA-454/R-93-047
Xylenes	EPA-454/R-93-048

Methyl Ethyl Ketone	EPA-454/R-93-046
Methyl Chloroform	EPA-454/R-93-045
Chlorobenzene (Update)	EPA-454/R-93-044
Benzene Update	Draft
Polycyclic Organic matter (POM) Update	Draft
1,3-Butadiene Update	EPA-454/R-96-008
Lead	Draft
Arsenic	Draft

This document deals specifically with an update of the previous document on emissions of mercury and mercury compounds (EPA-454/R-93-023); however, the majority of the information contained in this document concerns elemental mercury emissions.

In addition to the information presented in this document, another potential source of emissions data for mercury and mercury compounds is the Toxic Chemical Release Inventory (TRI) form required by Section 313 of Title III of the 1986 Superfund Amendments and Reauthorization Act (SARA 313). SARA 313 requires owners and operators of facilities in certain Standard Industrial Classification Codes that manufacture, import, process or otherwise use toxic chemicals (as listed in Section 313) to report annually their releases of these chemicals to all environmental media. As part of SARA 313, EPA provides public access to the annual emissions data. The TRI data include general facility information, chemical information, and emissions data. Air emissions data are reported as total facility release estimates for fugitive emissions and point source emissions. No individual process or stack data are provided to EPA under the program. The TRI requires sources to use stack monitoring data for reporting, if available, but the rule does not require stack monitoring or other measurement of emissions if data from these activities are unavailable. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment.

The reader is cautioned that the TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment studies. In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). We recommend the use of TRI data in conjunction with the information provided in this document to locate potential emitters of mercury and to make preliminary estimates of air emissions from these facilities.

Mercury is of particular importance as a result of the Clean Air Act Amendments of 1990 (CAAA). Mercury and mercury compounds are included in the Title III list of hazardous air pollutants (HAPs) and will be subject to standards established under Section 112, including maximum achievable control technology (MACT). Also, Section 112(c)(6) of the 1990 CAAA mandate that mercury (among others) be subject to standards that allow for the maximum degree of reduction of emissions. These standards are to be promulgated no later than 10 years following the date of enactment. In addition to Section 112(c)(b), other sections of the CAAA that may require data on mercury emissions include the electric utility steam-generating units, Section 112(n)(1)(A); the National Institute of Environmental Health Sciences (NIEHS) health effects study, Section 112(n)(1)(B); the mercury report to Congress, Section 112(n)(1)(C); the Great Waters Program, Section 112(m); the National Academy of Sciences (NAS) risk assessment methodology study, Section 112(o)(1); the area source program, Section 112(k); and the solid waste combustion program, Section 129.

The data on mercury emissions are based, whenever possible, on the results of actual test procedures. Data presented in this document are total mercury emissions and do not differentiate the chemical forms of the mercury. The sampling and analysis procedures employed for the determination of the mercury concentrations from various sources are presented in Section 9, Source Test Procedures. These procedures do not provide data on the speciation of the mercury in the emissions.

2.0 OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of mercury and mercury compounds and estimating air emissions from these sources. The information summarized in this document should not be assumed to represent the source configuration or emissions of any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this document. As stated in Section 1, this document represents a revision and update of the locating and estimating document on mercury and mercury compounds published in 1993. In addition to an update of the emission estimates, some sources were deleted and new sources were added. Previous sections on natural gas combustion and oil shale retorting were deleted from this document. Mercury emissions estimates from natural gas combustion were based on a single test report and the accuracy of the data in that report have been questioned. Oil shale retorting was deleted because it is not conducted in the United States. New sections have been added for hazardous waste incineration, pulp and paper production, and municipal waste landfills.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of mercury and mercury compounds and an overview of their production and uses. A chemical use tree summarizes the quantities of mercury produced by various techniques as well as the relative amounts consumed by various end uses. To the extent possible, the emissions data are presented for the 1994/1995 time period. This background section may be useful to someone who wants to develop a general perspective on the nature of the substance and where it is manufactured and used.

Sections 4 to 7 of this document focus on the major industrial source types that emit mercury. Section 4 discusses the production of mercury and mercury compounds. Section 5 discusses the different uses of mercury as an industrial feedstock. Section 6 discusses emissions from combustion sources. Section 7 discusses emissions from miscellaneous manufacturing processes, and Section 8 discusses emissions from miscellaneous fugitive and area sources. For each major industrial source category described, process descriptions and flow diagrams are given wherever possible, potential emission points are identified, and available emission factor estimates are presented that show the potential for mercury emissions before and after controls are employed by industry. Individual companies are named that are reported to be involved with the production and/or use of mercury based on industry contacts, reference materials, the Toxic Release Inventory (TRI), and available trade publications.

Section 9 of this document summarizes available procedures for source sampling and analysis of mercury. Details are not provided nor is any EPA endorsement given or implied for any of these sampling and analysis procedures. Section 10 provides references. Appendix A presents calculations used to derive the estimated 1994/1995 nationwide mercury emissions. Appendix B presents a summary of the combustion source test data. Appendix C lists U.S. Portland cement manufacturers. Appendix D presents U.S. crude oil distillation capacity. Appendix E presents 1994 U.S. pulp and paper mills.

This document does not contain any discussion of human health or environmental impacts of mercury, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the content or usefulness of this document are welcome, as is any information on process descriptions, operating practices, control measures, and emissions that would enable EPA to improve the document. All comments should be sent to:

Leader, Emission Factor and Inventory Group (MD-14)
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

3.0 BACKGROUND

3.1 NATURE OF THE POLLUTANT

Mercury, also called quicksilver, is a heavy, silver-white metal that exists as a liquid at ambient temperatures. Its chemical symbol, Hg, comes from the Latin word, hydrargyrum, meaning liquid silver. Mercury and its major ore, cinnabar (HgS), have been known and used for thousands of years. Table 3-1 summarizes the major chemical and physical properties of mercury.¹

Mercury metal is widely distributed in nature at very low concentrations. In uncontaminated soil, mercury concentrations range from 30 to 500 parts per billion (ppb) with an average of about 100 ppb. For most rocks, the mercury content ranges from 10 to 20,000 ppb. Except where special geologic conditions prevail or where anthropogenic sources lead to increases, surface fresh waters generally contain less than 0.1 ppb total mercury, and seawater averages 0.1 to 1.2 ppb of mercury.

Metallic mercury can be found in small quantities in some ore deposits; however, it usually occurs as a sulfide. It occurs sometimes as the chloride or the oxide, typically in conjunction with base and precious metals. Although HgS is by far the predominant mercury mineral in ore deposits, other common mercury-containing minerals include corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$), livingstonite (HgSb_4S_7), montroydite (HgO), terlinguaite (Hg_2OCl), calomel (HgCl), and metacinnabar, a black form of cinnabar.

Because metallic mercury has a uniform volume expansion over its entire liquid range and a high surface tension, it is used in barometers, manometers, thermometers, and other measuring devices. It also is used extensively in electrical applications, including batteries, electrical lamps, and wiring and switching devices. Its low electrical resistivity makes it one of the best electrical conductors among the metals.

In the ionic form, mercury exists in one of two oxidation states (or valences): Hg(I), or the mercurous ion, and Hg(II), or the mercuric ion. Of the two states, the higher oxidation state, Hg(II), is the more stable.

Mercury has a tendency to form alloys or amalgams with almost all metals except iron, although at higher temperatures it will even form alloys with iron. Mercury forms amalgams with vanadium, iron, niobium, molybdenum, cesium, tantalum, or tungsten to produce metals with good to excellent corrosion resistance. A mercury-silver amalgam traditionally has been used for teeth fillings.

Mercury is stable at ambient temperatures. It does not react with air, ammonia, carbon dioxide, nitrous oxide, or oxygen but readily combines with the halogens and sulfur. Mercury will react with any hydrogen sulfide present in the air and should be kept in covered containers. It is not affected by hydrochloric acid but is attacked by concentrated sulfuric acid. Mercury can be dissolved in either dilute or concentrated nitric acid, resulting in the formation of either mercurous [Hg(I)] salts (if the mercury is in excess or no heat is applied) or mercuric [Hg(II)] salts (if excess acid or heat is used).

3.2 OVERVIEW OF PRODUCTION, USE, AND EMISSIONS

3.2.1 Production

Primary production of mercury occurs principally as a byproduct of gold mining. Mercury was previously mined from mercury ores in Nevada, but that mine closed in 1990. It is still produced in relatively small quantities as a byproduct from gold ores in Nevada, California, and Utah.²

Secondary production (recycling) of mercury includes the processing of scrapped mercury-containing products, and industrial waste and scrap. Sales of scrap mercury from U.S. Government

TABLE 3-1. PHYSICAL AND CHEMICAL PROPERTIES OF MERCURY

Property	Value
Atomic weight	200.59
Crystal system	Rhombohedral
CAS registry number	7439-97-6
Atomic number	80
Valences	1, 2
Outer electron configuration	5d ¹⁰ 6s ²
Ionization potentials, normal, eV	
1st electron	10.43
2nd electron	18.75
3rd electron	34.20
Melting point, °C	-38.87
Boiling point, °C	356.9
Latent heat of fusion, J/g (cal/g)	11.80 (2.8)
Latent heat of vaporization, J/g (cal/g)	271.96 (65.0)
Specific heat, J/g (cal/g)	
Solid	
-75.6°C	0.1335 (0.0319)
-40°C	0.141 (0.0337)
-263.3°C	0.0231 (0.00552)
Liquid	
-36.7°C	0.1418 (0.0339)
210°C	0.1335 (0.0319)
Electrical resistivity, Ω-cm, at 20°C	95.8 x 10 ⁻⁶
Density, g/cm ³	
at 20°C	13.546
at melting point	14.43
at -38.8°C (solid)	14.193
at 0°C	13.595
Thermal conductivity, W/(cm ² ·K)	0.092
Vapor pressure, 25°C	2 x 10 ⁻³ mm Hg
Solubility in water, 25°C	20-30 µg/L

Source: Reference 1.

stockpiles were a major secondary source of mercury until July 1994 when Congress suspended sales.² Major sources of recycled mercury are dental amalgams, scrap mercury from instrument and electrical manufacturers (including fluorescent lamps), wastes and sludges from research laboratories and electrolytic refining plants, and mercury batteries.¹

Table 3-2 presents the 1991 to 1995 supply-and-demand figures for mercury. The information contained in Table 3-2 was obtained from the U.S. Geological Survey.² Values for secondary production, industry stocks, and industrial consumption are based on voluntary response to USGS questionnaires. The values presented are based on limited questionnaire response and USGS estimates. As shown in Table 3-2, the total U.S. supply of mercury in 1995 was 911 Mg (1,002 tons). An estimated 59 percent of the total supply resulted from primary and secondary mercury production processes. Table 3-2 also shows that of the total 1995 U.S. mercury supply, approximately 48 percent (436 Mg [480 tons]) was used to meet domestic demands, while 20 percent met export demands.

The supply-and-demand figures presented in Table 3-2 illustrate a dramatic change in the overall structure of the industrial demand for mercury in the U.S. Since 1992, U.S. industrial demand for mercury has steadily declined from 621 Mg (683 tons) to 436 Mg (480 tons), a decrease of 30 percent. U.S. exports of mercury have undergone greater decline, falling from 977 Mg (1,075 tons) to 179 Mg (197 tons), a reduction of over 80 percent. Conversely, imports of mercury have risen from 56 Mg (62 tons) in 1991 to 377 Mg (415 tons) in 1995, an increase of 673 percent. The decline of mercury exports and the sharp increase in mercury imports are due in large part to the suspension by Congress of sales of mercury from U.S. Government stockpiles.

3.2.2 End-Use

Table 3-3 summarizes the end-use pattern for industrial consumption of mercury in the U.S. in 1991, 1994, and 1995.² The percentage of the total 1995 mercury supply for industrial consumption that was consumed by each end-use category is shown in Figure 3-1. The chlor-alkali industry, at 35.3 percent, accounts for the largest percentage consumption of mercury. Wiring devices and switches manufacture and measuring and control instruments manufacture represent the second and third largest consumers of mercury at 19.3 percent and 9.9 percent, respectively. The remaining source categories, as outlined in Table 3-3, account for approximately 35 percent of total industrial mercury consumption in 1995.²

During the period from 1991 to 1995, the demand picture for mercury has continued to undergo significant change in the overall demand among industries. The magnitude of these overall changes and the dramatic change in mercury demand for specific industries is shown in Table 3-3. The most dramatic change occurred in the battery manufacturing industry where demand dropped from 78 Mg (86 tons) in 1991, to less than 0.5 Mg (0.6 tons) in 1995. Other industries showing significant decreases in demand from 1991 levels were measuring and control instrument manufacture and chlorine production.²

Three industries showed an increase in mercury consumption from 1991 to 1995. The most significant increase occurred in the wiring devices and switches industry, where demand rose from 25 Mg (27.5 tons) in 1991 to 84 Mg (92.4 tons) in 1995. The dental equipment and supplies industry also underwent a significant increase in mercury demand, rising from 27 Mg (29.7 tons) in 1991 to 32 Mg (35.2 tons) in 1995. The only other industry exhibiting an increase in mercury demand is the electric lighting industry with a slight increase from 29 Mg (31.9 tons) in 1991 to 30 Mg (33 tons) in 1995. Despite the increases in these three industries, the net change in total U.S. demand for mercury from 1991 to 1995 is a decrease of 118 Mg (130 tons) or 21 percent from the 1991 level.

The demand decreases in end-use areas will affect the magnitude of mercury emissions in the U.S. and will lead to secondary impacts. One secondary impact on emissions will be in the area of waste disposal, particularly in municipal and medical waste combustion. In medical waste, used batteries constitute a major source of mercury emissions during incineration. Mercury use in battery production decreased by over 99 percent from 1991 to 1995. This decrease should be evident in mercury emissions from both medical waste and municipal waste incineration. In addition, the significant decrease in demand for the measuring and control instruments industry may also be felt in emissions from municipal waste incineration. This impact would occur further in the future than the impact from batteries because of the longer equipment life expectancy.

TABLE 3-2. U.S. SUPPLY AND DEMAND FOR MERCURY, 1991 TO 1995
(metric tons, Mg)^a

	1991	1992	1993	1994	1995
Supply:					
No. of producing mines	8	9	9	7	8
Mine production, byproduct	58	64	W ^b	W	W
Secondary production:					
Industrial	165	176	350	466	534
Government ^c	215	103	---	---	---
Shipments from NDS ^d	103	267	543	86	0
Imports for consumption	56	92	40	129	377
Total supply ^e	597	702	933	681	911
Demand:					
Industrial consumption	554	621	558	483	436
Exports	786	977	389	316	179
Total demand ^e	1,340	1,598	947	799	615

Source: Reference 2.

^aFor values in U.S. short tons, multiply metric tons (Mg) by 1.1.

^bW = Withheld to avoid disclosing company proprietary data.

^cSecondary mercury shipped from U.S. Department of Energy stocks.

^dPrimary mercury shipped from the National Defense Stockpile.

^eFrom the table it is obvious that the supply and demand figures do not agree. In discussions of this discrepancy with J. Plachy (U.S.G.S), he indicated confidence in all figures in this table except industrial consumption. The individual consumption figures are based in large part on U.S.G.S. estimates and constitute the greatest area of uncertainty.

TABLE 3-3. END-USE PATTERN OF MERCURY FOR INDUSTRIAL CONSUMPTION

Industry	Mercury demand, Mg ^a		
	1991	1994	1995
Chlorine production	184	135	154
Wiring devices and switches	25	79	84
Measuring and control instruments	70	53	43
Dental equipment and supplies	27	24	32
Electric lighting	29	27	30
Other chemical and allied products ^b	18	25	^c
Laboratory uses	10	24	^c
Batteries	78	6	<0.5
Paint	6	^d	^d
Other uses ^e	107	110	93
Total demand	554	483	436

Source: Reference 2.

^aFor values in U.S. short tons, multiply metric tons (Mg) by 1.1.

^bIncludes pharmaceutical uses and miscellaneous catalysts.

^cWithheld to avoid disclosing company proprietary data; included in "Other uses."

^dNot reported separately.

^eIncludes other electrical and electronic uses, other instruments and related products, and unclassified uses. For 1995, it also includes "Laboratory uses" and "Other chemical and allied products."

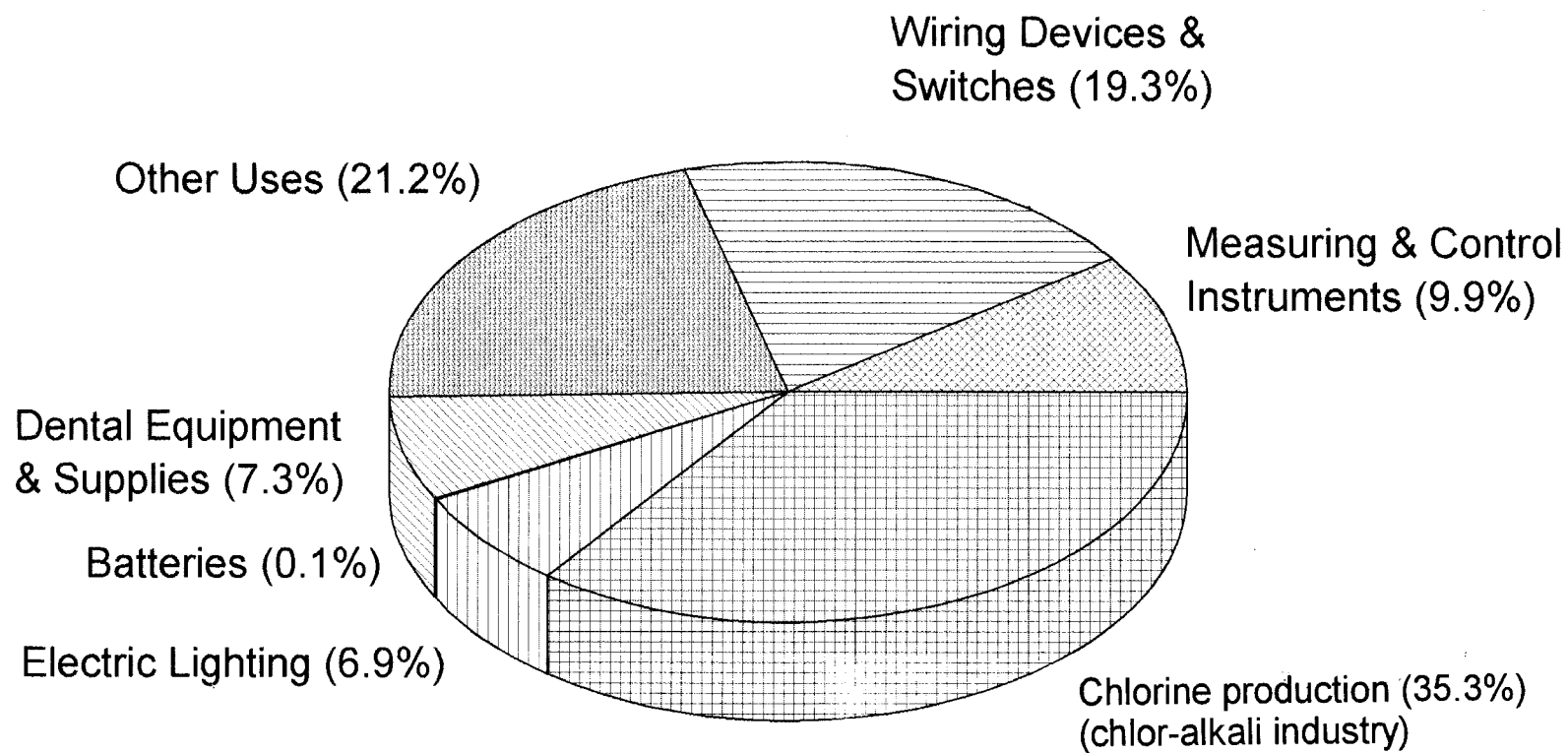


Figure 3-1. End-use pattern of mercury²

3.2.3 Emissions

The source of emissions information used to determine a portion of the source categories is the 1994 Toxic Chemicals Release Inventory System (TRI) form required by Section 313 of Title III of the 1986 Superfund Amendments and Reauthorization Act (SARA 313).³ This section requires owners and operators of Federal facilities and facilities in Standard Industrial Classification (SIC) codes 20-39 that manufacture, import, process, or otherwise use toxic chemicals to report their annual air releases of these chemicals. All facilities in these SIC's are not required to report; there are thresholds concerning the number of full-time equivalent employees and quantity of the compound used, below which facilities are not required to report releases. The emissions are to be based on source tests (if available); otherwise, emissions may be based on emission factors, mass balances, or other approaches. Certain source categories (e.g., combustion sources) that account for substantial mercury emissions, but which are not reported in TRI, were included in the estimates presented.

It should be noted that, in selected cases, facilities reported to TRI under multiple SIC codes. As a result, it was difficult to assign emissions to a specific SIC code. In this case, efforts were made to determine the appropriate SIC codes associated with the emissions. However, if that was not possible, the data were not used in the analysis. Other reference sources provided additional potential emission source categories that may not have been included in TRI.⁴

Another source of emissions information used to determine annual emissions from several of the source categories is information collection requests authorized under Section 114 of the Clean Air Act Amendments of 1990 (CAAA). These requests for information are distributed primarily for the purpose of developing or assisting in the development of implementation plans under Section 110, standards of performance under Section 111, or emission standards under Section 112 of the CAAA. These requests are typically in the form of a questionnaire and often request detailed information on air emissions, control technologies, and related process parameters.

Table 3-4 provides a summary of the estimated 1995 nationwide mercury emissions for those source types where adequate information was available (i.e., emission factors and production data). Appendix A presents the data used for each of these estimates, assumptions, and the emission calculations for each category of these source types. The estimated emissions were based on emission factors provided in this document or calculated from source test data and appropriate process information, if available.

The total 1995 nationwide mercury emissions estimate was 140 Mg (154 tons) for those source types identified in Table 3-4. The three specific categories emitting the largest quantities of mercury were coal combustion (67.8 Mg [74.6 tons]), municipal waste combustion (26 Mg [29 tons]), and medical waste combustion (14.5 Mg [16.0 tons]). These three specific categories combined accounted for approximately 78 percent of the total mercury emissions listed in Table 3-4.

Of the five major source types, mercury emissions resulting from combustion categories accounted for a total of 123.0 Mg (135.6 tons), or approximately 88 percent of the total estimated emissions. Within the combustion group, the major contributor to mercury emissions was from the combustion of coal, followed by municipal waste, and medical waste. Coal combustion accounted for 55 percent of the total emissions from combustion sources and 48 percent of the total emissions from all source types. The other six combustion areas, wood, municipal waste, medical waste, hazardous waste, sewage sludge, and oil, collectively accounted for 45 percent of the total emissions from combustion groups and 39 percent of the total emissions from all source types.

TABLE 3-4. ESTIMATED 1994-1995 NATIONWIDE MERCURY EMISSIONS
FOR SELECTED SOURCE CATEGORIES

Source type	Mercury emissions		Basis ^a
	Mg	Tons	
Mercury and mercury compound production			
Primary mercury production	NA		No longer mined
Secondary mercury production	0.13	0.14	Emission factor
Mercury compound production	NA		No emission factors
Major uses of mercury			
Chlorine production	6.5	7.1	1994 TRI report
Battery manufacture	5E-04	6E-04	Emission factor
Electrical uses	0.4	0.5	Emission factor
Measurement/control instruments	0.4	0.4	Emission factor
Combustion sources			
Coal combustion	67.8	74.6	Emission factor/EMF factor
Oil combustion	7.6	8.4	Emission factor
Municipal waste combustion	26	29	Capacity data/F-factors
Sewage sludge combustion	0.9	0.9	Emission factors
Hazardous waste combustion ^b	6.3	6.9	EPA/OSW estimates
Medical waste combustion ^b	14.5	16.0	Capacity data/F-factors
Wood combustion ^c	0.1	0.1	Emission factor
Miscellaneous manufacturing processes			
Portland cement production	4.0	4.4	Emission factor
Lime manufacturing	0.1	0.1	Emission factor
Carbon black production	0.3	0.3	Emission factor
Byproduct coke production ^d	0.6	0.7	Emission factor
Primary lead smelting	0.1	0.1	Raw materials
Primary copper smelting	0.06	0.06	Plant data
Petroleum refining	NA		No emission factor
Municipal solid waste landfills	0.07	0.08	Test data
Geothermal power plants ^e	1.3	1.4	Emission factor
Pulp and paper production	1.6	1.8	Emission factor
Other miscellaneous sources			
Mercury catalysts	NA		No production data
Dental alloys	0.6	0.7	Emission factor
Mobile sources	NA		No emission factor
Crematories	0.7	0.8	Emission factor
Paint	NA		No emission factor
TOTAL	140	154	

NA = Not applicable.

^aSee Appendix A for details of the estimation procedure.

^bEmissions summary year not provided.

^cEmissions based on 1980 wood-fired boiler capacity.

^dEmissions based on 1991 production capacity.

^eEmissions based on 1993 capacity.

4.0 EMISSIONS FROM MERCURY PRODUCTION

In 1995, the total supply of metallic mercury (Hg) in the United States was estimated to be 1,045 Mg (1,152 tons)². Of this total, approximately 51 percent resulted from secondary production processes (industrial reclamation); 36 percent was due to imports; about 2 percent was from shipments from the National Defense Stockpile; and 11 percent was from industry stocks (see Section 3, Figure 3-1). There were 16 facilities in the United States that produced mercury. Of these facilities, eight produced mercury as a byproduct from gold ore, and eight were secondary mercury production facilities that reclaim mercury. Mercury emissions occur primarily during the metal production process and during mercury reclamation processes. In this section, mercury emissions were estimated only for mercury reclamation; no data were available for the other source types. For mercury reclamation, the mercury emissions for 1994 were estimated to be 0.13 Mg (0.14 tons).

This section presents information on the identification of the producers and descriptions of typical production processes. Process flow diagrams are given as appropriate, and known emission control practices are presented. Estimates of mercury emissions are provided in the form of emission factors wherever data were available.

4.1 PRIMARY MERCURY PRODUCTION

Mercury is currently produced in the United States only as a byproduct from the mining of gold ores. Production from mercury ore had occurred at the McDermitt Mine in McDermitt, Nevada, but the mine ceased operation in 1990. In 1995, eight U.S. gold mines produced metallic mercury as a byproduct; Table 4-1 presents a list of these mines. As shown in the table, six of the mines are in Nevada, one is in California, and one is in Utah. None of the operating gold mines in Alaska produce byproduct mercury. In 1995, the total quantity of mercury recovered at these mines was withheld to avoid disclosing company proprietary data.²

TABLE 4-1. BYPRODUCT MERCURY-PRODUCING GOLD MINES IN THE UNITED STATES IN 1995

Mine	County and State	Operator
Getchell	Humboldt, NV	FMC Gold Co.
Carlin Mines Complex	Eureka, NV	Newmont Gold Co.
Alligator Ridge	White Pine, NV	Placer Dome U.S.
Enfield Bell	Elko, NV	Independence Mining Co., Inc.
McLaughlin	Napa, CA	Homestake Mining Co.
Mercur ^a	Tooele, UT	Barrick Mercur Gold Mines, Inc.
Paradise Peak	Gabbs, NV	FMC Gold Co.
Pinson Mine	Humboldt, NV	Pinson Mining Co.

Source: Reference 2.

^aMine closed in 1997.

In 1994, 86 Mg (95 tons) of primary mercury were shipped from the National Defense Stockpile.² Because of a suspension of sales in 1994, there were no sales from the stockpile in 1995.

4.1.1 Process Description

4.1.1.1 Production from Mercury Ores. No process description of the McDermitt Mine operation will be presented because the existing equipment has been removed from the site, thereby negating any possibility that the facility could reopen at a future date using the same process and equipment.

4.1.1.2 Byproduct from Gold Ores. Recovery of mercury as a byproduct from gold ores is the only remaining ore-based production process; all other processes for mercury production are either reclamation or government surplus stock. A simplified flow diagram depicting mercury recovery from a gold cyanidation process is shown in Figure 4-1. The flow diagram and process description for mercury recovery from gold mining is not intended to reflect any specific gold mine operation but to summarize the types of processes and controls that could be employed. Actual processes will vary from mine to mine.

The incoming gold ore is crushed using a series of jaw crushers, cone crushers, and ball mills. If the incoming ore is an oxide-based ore, no pretreatment is required, and the crushed ore is mixed with water and sent to the classifier. If the ore is a sulfide-based ore, it must be pretreated using either a fluidized-bed or multiple hearth pretreatment furnace (roaster) to convert metallic sulfides to metallic oxides.⁵ The exhaust gas from either of these units is sent through wet electrostatic precipitators (ESP's) and, if necessary, through carbon condensers. The exhaust gas then passes through a scrubber in which SO₂ is removed by lime prior to discharging to the atmosphere. If the treated sulfide ore is high in mercury content, the primary mercury recovery process occurs from the wet ESP's. If the concentration is sufficiently low, no attempt is made to recover the mercury for sale. The pretreated ore is mixed with water and sent to the classifier, where the ore is separated (classified) according to size. Ore pieces too large to continue in the process are returned to the crusher operation.

From the classifier, the slurry passes through a concentrator to reduce the water content and then to a series of agitators containing the cyanide leach solution. From the agitators, the slurry is filtered, the filter cake is sent to disposal, and the filtrate containing the gold and mercury is transferred to the electrowinning process. If the carbon-in-pulp (CIP) process is used, the cyanide pulp in the agitators is treated with activated carbon to adsorb the gold and mercury. The carbon is filtered from the agitator tanks and treated with an alkaline cyanide-alcohol solution to desorb the metals. This liquid then is transferred to the electrowinning tanks. In the electrowinning process, the gold and mercury are electrodeposited onto a stainless steel wool cathode, which is sent to a retort to remove mercury and other volatile impurities. The stainless steel wool containing the gold is transferred from the retort to a separate smelting furnace where the gold is melted and recovered as crude bullion.

The exhaust gas from the retort, containing mercury, SO₂, particulate, water vapor, and other volatile components, passes through condenser tubes where the mercury condenses as a liquid and is collected under water in the launders. From the launders, the mercury is purified and sent to storage. After passing through the condenser tubes, the exhaust gas goes through a venturi and impinger tower to remove particulate and water droplets and then moves through the SO₂ scrubber prior to discharging to the atmosphere.

Gold ores in open heaps and dumps also can be treated by cyanide leaching. In this process, the gold ore is placed on a leaching pad and sprayed with the cyanide solution. The solution permeates down through the ore to a collection system on the pad, and the resulting pregnant solution is sent to a solution pond. From this pond, the leachate liquors, which contain gold and mercury, are transferred to the gold recovery area where the liquor is filtered and sent to the electrowinning process.

4.1.2 Emission Control Measures

Potential sources of mercury emissions from gold processing facilities are at locations where furnaces, retorts, or other high temperature sources are used in the process and where the mercury is removed from the launders. The treated gas discharged to the atmosphere is also a source of mercury emissions. These sources are denoted in Figure 4-1 with a solid circle.

When pretreatment roasting is required, the exhaust gases from the furnace pass through a cyclone to remove particulate and then move through wet ESP's to remove arsenic, mercury, and some of the SO₂. If the mercury concentration in the gold ore is high, the ESP's will not remove all of the mercury, and an activated carbon adsorber bed may be required for additional mercury removal. The gas passes through a

Figure 4-1. Major components of mercury recovery from gold ores.

lime scrubber to remove SO_2 ; if the SO_2 concentration is low, a caustic scrubber may be used.⁵ From the scrubber, the gas is discharged through the stack to the atmosphere. Essentially the same emission control measures are used from the exhaust gas from the retort. After the gas passes through the condenser tubes to remove the mercury, a venturi and a cyclone are used to remove particulate and water droplets. These controls are followed by the lime scrubber to remove the SO_2 prior to discharging the clean gas to the atmosphere.

4.1.3 Emissions

The major sources of mercury emissions for gold processing facilities are the pretreatment roaster (if required) and the retort. Other sources of emissions are from the purification process after removal of mercury from the launders and the stack emissions to the atmosphere. No emissions data have been published for facilities producing mercury as a byproduct from gold ore. Limited data were published for emission sources at facilities that produced mercury from the primary ore.^{6,7} While treatment techniques to recover the mercury, after the mercury has been vaporized in a retort or furnace, and the emission sources are very similar to production from primary ore, the overall production process is considerably different. The emission factors for production from primary ore should not be used to estimate emissions from gold mining operations.

4.2 SECONDARY MERCURY PRODUCTION

There are two basic categories of secondary mercury production: recovery of liquid mercury from dismantled equipment and mercury recovery from scrap products using extractive processes. On an annual basis, the total quantity of mercury recovered as liquid mercury is much greater than that recovered by extractive processes. Three areas that have contributed to a large proportion of the liquid mercury recovery category are: (1) dismantling of chlorine and caustic soda manufacturing facilities; (2) recovery from mercury orifice meters used in natural gas pipelines; and (3) recovery from mercury rectifiers and manometers. In each of these processes, the liquid mercury is drained from the dismantled equipment into containers and sold on the secondary mercury market. The second category involves the processing of scrapped mercury-containing products and industrial wastes and sludges using thermal or chemical extractive processes because the mercury cannot be decanted or poured from the material. One mercury recycler (Bethlehem Apparatus Company) estimated that this second category accounted for 15 to 20 percent of the total quantity of mercury reported as recycled from industrial scrap in 1995.

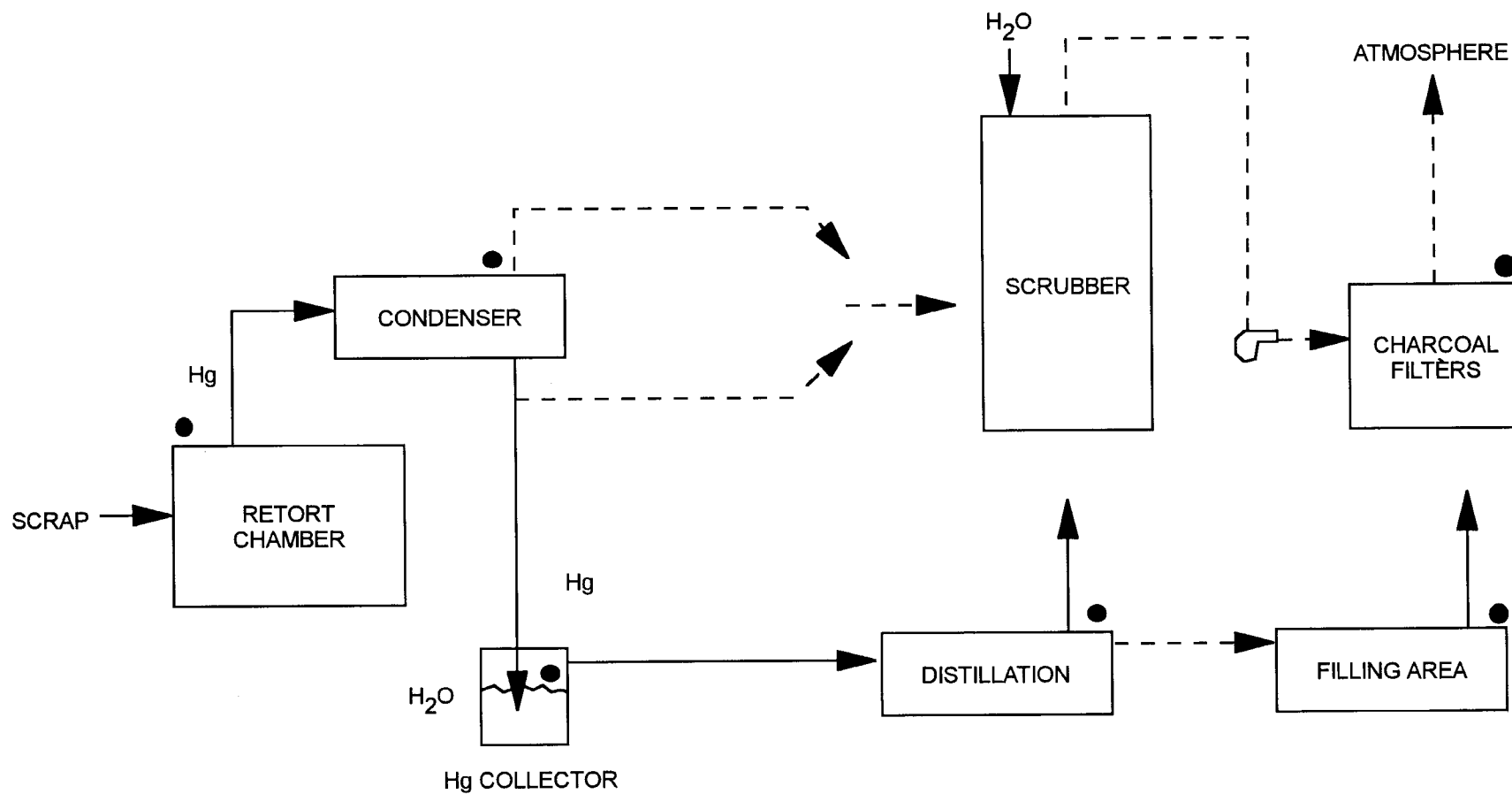
In 1995, an estimated 534 Mg (588 tons) of mercury was recycled from industrial scrap.² These totals do not include in-house mercury reclamation at industrial plants using mercury. According to the USGS, eight major companies were reported to be involved in secondary mercury production using purchased scrap material (mercury recyclers) in 1995.² The three dominate companies in this market are Bethlehem Apparatus Company in Hellertown, Pennsylvania; D. F. Goldsmith in Evanston, Illinois; and Mercury Refining Company in Albany, New York.

4.2.1 Process Description

The predominant method to recover metallic mercury for recycling from scrap products is thermal treatment.¹ Figure 4-2 provides a general process diagram for secondary mercury recovery at a battery plant.⁸ This process is generally representative of the recovery of mercury by thermal treatment of scrap. Generally, the mercury-containing scrap is reduced in size and is heated in retorts or furnaces at about 538°C (1000°F) to vaporize the mercury. The mercury vapors are condensed by water-cooled condensers and collected under water.⁸

Vapors from the condenser, which may contain particulate, organic compounds, and possibly other volatile materials from the scrap, are combined with vapors from the mercury collector line. This combined vapor stream is passed through an aqueous scrubber to remove particulate and acid gases (e.g., HCl , SO_2). From the aqueous scrubber, the vapor stream passes through a charcoal filter to remove organic components prior to discharging into the atmosphere.

The collected mercury is further purified by distillation, collected, and then transferred to the filling area. In the filling area, special filling devices are used to bottle small quantities, usually 0.464 kg (1 lb) or 2.3 kg (5 lb) of distilled mercury. With these filling devices, the mercury flows by gravity through tubing from a holding tank into the flask until the flask overflows into an overflow bottle.



● DENOTES POTENTIAL MERCURY EMISSION SOURCE

Figure 4-2. Process flow diagram for secondary recovery at a battery plant.

The desired amount of mercury is dispensed into the shipping bottle by opening a valve at the bottom of the flask. The shipping bottle is then immediately capped after the filling and sent to the storage area.⁸

4.2.2 Emission Control Measures

Information on specific emission control measures is very limited and site specific. If a scrubber is used, as shown in Figure 4-2, mercury vapor or droplets in the exhaust gas may be removed by condensation in the spray. There is no information to indicate that chemical filters would be effective in removing mercury vapors. No information was found for other control measures that are used in secondary mercury production processes. Concentrations in the workroom air due to mercury vapor emissions from the hot retort may be reduced by the following methods: containment, local exhaust ventilation, dilution ventilation, isolation, and/or personal protective equipment. No information was provided to indicate that these systems are followed by any type of emission control device.⁸ Vapor emissions due to mercury transfer during the distillation or filling stages may be reduced by containment, ventilation (local exhaust or ventilation), or temperature control.

4.2.3 Emissions

During production of mercury from waste materials using an extractive process, emissions may vary considerably from one type of process to another. Emissions may potentially occur from the following sources: retort or furnace operations, distillation, and discharge to the atmosphere from the charcoal filters. The major mercury emission sources are due to condenser exhaust and vapor emissions that occur during unloading of the retort chamber. These sources are indicated in Figure 4-2 by a solid circle. Mercury emissions also can occur in the filling area when the flask overflows and during the bottling process.^{8,9}

Mercury Refining Company reported results from two emission test studies conducted in 1994 and 1995 that showed average mercury emissions of 0.85 kg/Mg (1.7 lb/ton) of mercury recovered.¹⁰ In 1973, emission factors were estimated to be 20 kg (40 lb) per megagram (ton) of mercury processed due to uncontrolled emissions over the entire process.⁶

Mercury emission data were reported in the 1994 TRI only for Mercury Refining Company, Inc., in Albany, New York, and Bethlehem Apparatus Company in Hellertown, Pennsylvania.³ Mercury Refining reported plant emissions to the atmosphere of 116 kg (255 lb) for 1994, and Bethlehem Apparatus reported plant emissions to the atmosphere of 9 kg (20 lb) for 1994. The other major recycler, D. F. Goldsmith, does not use extractive processes; their recycling is primarily from purchases of mercury decanted from old equipment. Mercury emission data were not available for the other five facilities.

The total mercury emissions were estimated to be 0.13 Mg (0.14 tons) for 1994; see Appendix A for calculations.

4.3 MERCURY COMPOUNDS PRODUCTION

The production of mercury compounds presents a potential source of release of mercury into the atmosphere. Table 4-2 lists several producers of inorganic mercury compounds. No U.S. producers of phenylmercury acetate (PMA) or thimerosal (merthiolate) were identified.¹¹ No facility reported mercury emissions in the 1994 TRI.³

TABLE 4-2. MERCURY COMPOUND PRODUCERS

Producer	Location	Compound(s)
Elf Atochem North America, Inc., Chemical Specialties Division	Tulsa, OK	HgF ₂ , Hg ₂ F ₂
GFS Chemicals, Inc.	Columbus, OH	HgBr ₂ , HgI ₂ , Hg(NO ₃) ₂ , HgSO ₄
Johnson Matthey, Inc.	Ward Hill, MA	Hg ₂ (NO ₃) ₂
R.S.A Corporation	Danbury, CT	Hg(SCN) ₂

Source: Reference 11.

4.3.1 Process Description

Numerous inorganic mercury compounds are produced annually in the United States using metallic mercury as the starting material. The production processes for mercuric chloride and mercuric oxide were selected to serve as typical examples. The production processes for each compound have been studied at Troy Chemical Corporation.¹² A synopsis of these two production processes is provided below; additional information can be found in Reference 8.

4.3.1.1 Mercuric Chloride and Mercurous Chloride. The production of these two compounds occurs by the direct reaction of mercury with chlorine gas according to the following equations:

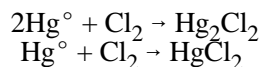


Figure 4-3 presents a process diagram for the production of mercuric chloride. Elemental mercury (Stream A) is pumped from a holding tank into a reactor where it reacts with excess chlorine gas (Stream B). The reaction products (Stream C) are ducted to a precipitation unit where the dry product (HgCl_2) settles and is raked out. Mercuric chloride (Stream D) is packaged and sealed in drums for shipping.^{8,12} The exhaust from the reactor (Stream E) is sent to a caustic scrubber where unreacted mercury is recovered and is then recycled back (Stream F) to the reactor. A similar process is used to produce mercurous chloride.

4.3.1.2 Mercuric Oxide. Two different processes have been used for mercuric oxide production: (1) production via mercuric chloride and (2) production via mercuric nitrate intermediates. Both processes are shown in Figure 4-4.

In production via mercuric chloride, mercury (Stream A) and chlorine in brine solution (Stream B) are mixed in a reactor where mercuric chloride is produced in solution by oxidation of the liquid mercury. The mercuric chloride (Stream C) is then transferred to a second reactor and an aqueous caustic (NaOH) solution is added, resulting in the formation of mercuric oxide. The mercuric oxide precipitate (Stream D) is then washed, dried, screened, and packaged⁹.

In the process using the mercuric nitrate intermediate, (also shown in Figure 4-4), mercury (Stream A) and nitric acid (Stream B) are combined in a reactor, resulting in the formation of mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$). The mercuric nitrate (Stream C) is then transferred to a second reactor where mercuric oxide is precipitated by adding an aqueous caustic solution (NaOH). The mercuric oxide (Stream D) is washed, dried, ground, and packaged.⁸

4.3.2 Emission Control Measures

No information was found on specific emission control devices to remove or treat the mercury emissions. Only methods designed to reduce the workplace concentrations without subsequent treatment were presented.⁸ Methods suitable for reducing workroom air concentrations of mercury during the production of mercury compounds are similar to those described for primary and secondary mercury processing. Particulate concentrations in the workplace resulting from several process operations (e.g., addition of dry chemicals to reactors, filtration, drying, grinding, and packaging) may be reduced by containment, exhaust ventilation, dilution ventilation, and personal protective equipment. Mercury vapor concentrations from mercury transfer to reactors and from the reactors may be reduced by containment.

During mercuric oxide production, grinding and packaging operations are done in an enclosed system under vacuum, including material transfers. A cyclone dust collector separates fine dust from product-sized HgO particles, which are channeled to the packaging station. The fine dust is collected and transferred periodically to fiber drums. The vacuum pump discharge also goes through a cyclone dust separator before it exhausts to the roof. Collected dust is recycled through the grinder.¹²

4.3.3 Emissions

During the production of these compounds, emissions of mercury vapor and particulate mercury compounds may occur at the following sources: reactors, driers, filters, grinders, and transfer operations. These emission sources are indicated in Figures 4-3 and 4-4 by a solid circle.

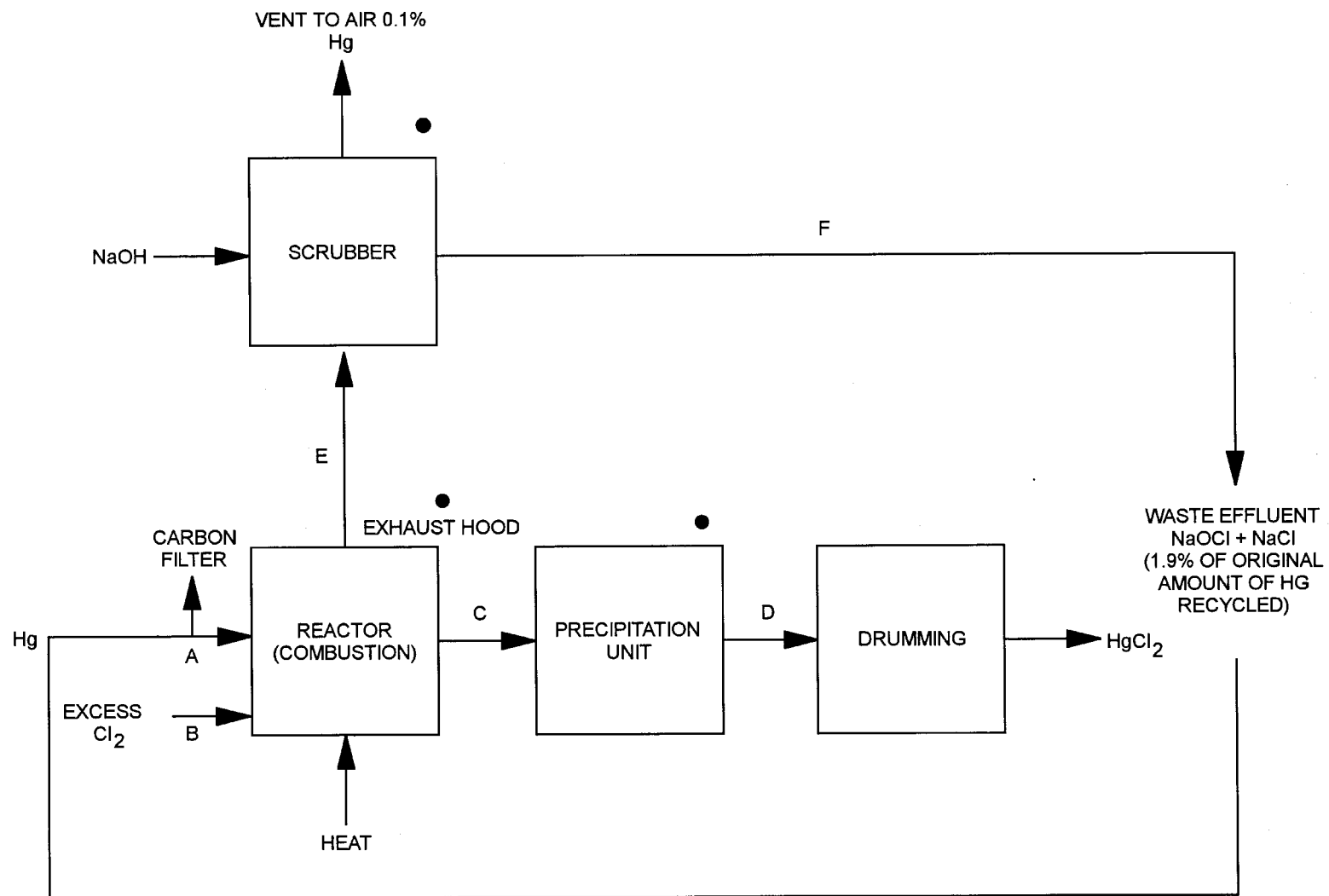


Figure 4-3. Mercuric/mercurous chloride production.

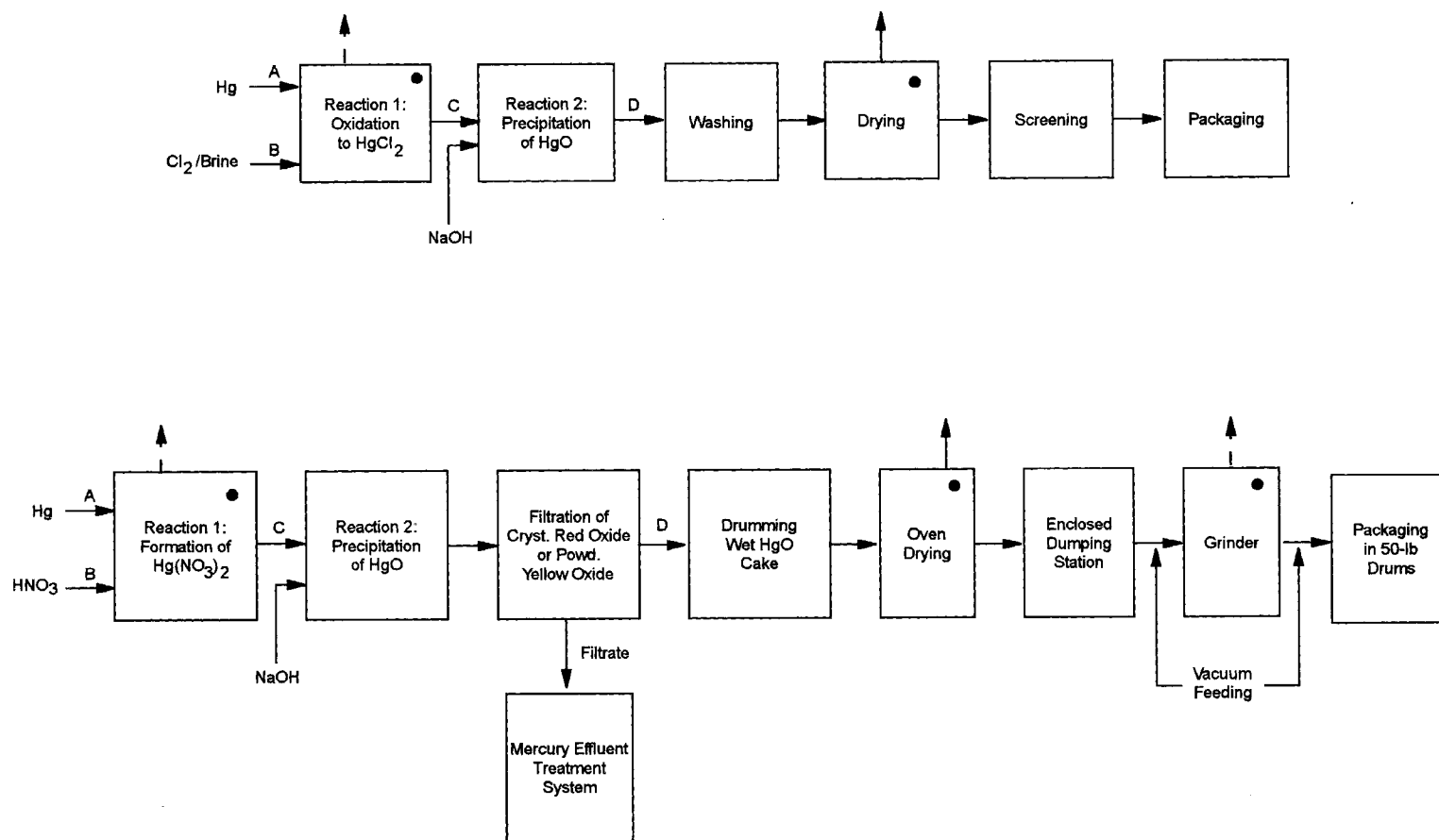


Figure 4-4. Mercuric oxide production via mercuric chloride and mercuric nitrate intermediates.

Emission factors are not available for production of mercury compounds. No test data for mercury emissions were found that would permit the calculation of emission factors.

5.0 EMISSIONS FROM MAJOR USES OF MERCURY

Emissions from industrial processes that use mercury are discussed in this section. The four commercial uses discussed in this section are (1) chlorine production using the mercury cell process, (2) primary battery production, (3) production of electrical lighting, wiring devices, and electrical switches, and (4) production of measuring and control instruments. A summary of the estimated mercury emissions from each of these industries is as follows:

Industry	Emissions, Mg (tons)
Chlorine production	6.5 (7.1)
Primary battery production	5 E-04 (6 E-04)
Electrical equipment production	0.4 (0.5)
Measurement/control instruments	0.4 (0.5)

This section is divided into four subsections, one devoted to each of the four commercial uses listed above. Each of the subsections presents a general discussion of the production process and where mercury is used in the process, descriptions of existing mercury emission control measures, and estimates of mercury emission factors. The level of detail varies according to the availability of information, particularly for emissions where data may be incomplete or absent.

5.1 CHLORINE PRODUCTION USING THE MERCURY CELL PROCESS

In 1996, the mercury cell process, which is the only chlor-alkali process using mercury, accounted for 12.1 percent of all U.S. chlorine production.¹³ Although most chlor-alkali plants use diaphragm cells, the mercury cell is still used at 14 facilities. The chlor-alkali industry, however, is gradually moving away from mercury cell production and toward a membrane cell process because the membrane cell process does not use mercury, is 12 to 14 percent more energy efficient, and produces mercury free products.¹⁴ Table 5-1 presents the location and capacity of mercury cell chlor-alkali production facilities operating in the U.S. in 1996.¹¹

5.1.1 Process Description

The mercury cell process consists of two electrochemical cells, the electrolyzer and the decomposer. A basic flow diagram for a mercury cell chlor-alkali production operation is shown in Figure 5-1.

Saturated (25.5 weight percent) purified sodium or potassium brine (Stream A) flows from the main brine saturation section, through the inlet end box, and into the electrolyzer cell. The cell is an elongated trough that is inclined approximately 1° to 2.5° with sides that are typically lined with rubber. The brine flows between stationary activated titanium anodes suspended from above into the brine; mercury, which is the cathode, flows concurrently with the brine over a steel base.

The electrochemical reaction that occurs at the titanium anodes is shown in equation (1); the reaction at the mercury cathode is shown in equation (2); and the overall reaction is shown in equation (3).



TABLE 5-1. 1996 MERCURY CELL CHLOR-ALKALI PRODUCTION FACILITIES

Facility ^a	Location ^a	Capacity ^b		1991 emissions, lb/yr ^c	1994 emissions, lb/yr ^d
		10 ³ Mg/yr	10 ³ tons/yr		
Ashta Chemicals, Inc.	Ashtabula, OH	36	40	N/A	1,660
Georgia-Pacific West, Inc.	Bellingham, WA	82	90	200	1,290
The BFGoodrich Company, BFGoodrich Specialty Chemicals	Calvert City, KY	109	120	1,206	842
Holtrachem Manufacturing Company	Reigelwood, NC	48	53	528	1,095
	Orrington, ME	76	80	735	582
Occidental Chemical Corporation, Basic Chemicals Group, Electrochemicals	Deer Park, TX	347	383	1,290	1,040
	Delaware City, DE	126	139	532	510
	Muscle Shoals, AL	132	146	184	233
Olin Corporation	Augusta, GA	102	112	1,540	1,317
	Charleston, TN	230	254	1,892	1,509
Pioneer Chlor-Alkali Company, Inc.	St. Gabriel, LA	160	176	1,240	N/A
PPG Industries, Inc., Chemicals Group	Lake Charles, LA	233	256	1,440	1,230
	New Martinsville, WV	70	77	1,085	1,130
Vulcan Materials Company, Vulcan Chemicals Division	Port Edwards, WI	65	72	1,030	N/A
TOTAL		1,816	1,998	12,902	12,438

^aReference 11.^bSRI figures adjusted based on questionnaire responses. References 11, 15-27.^cEmissions data based on responses to Section 114 information collection requests from the following: References 15-27.^dTRI emissions data. Reference 3.

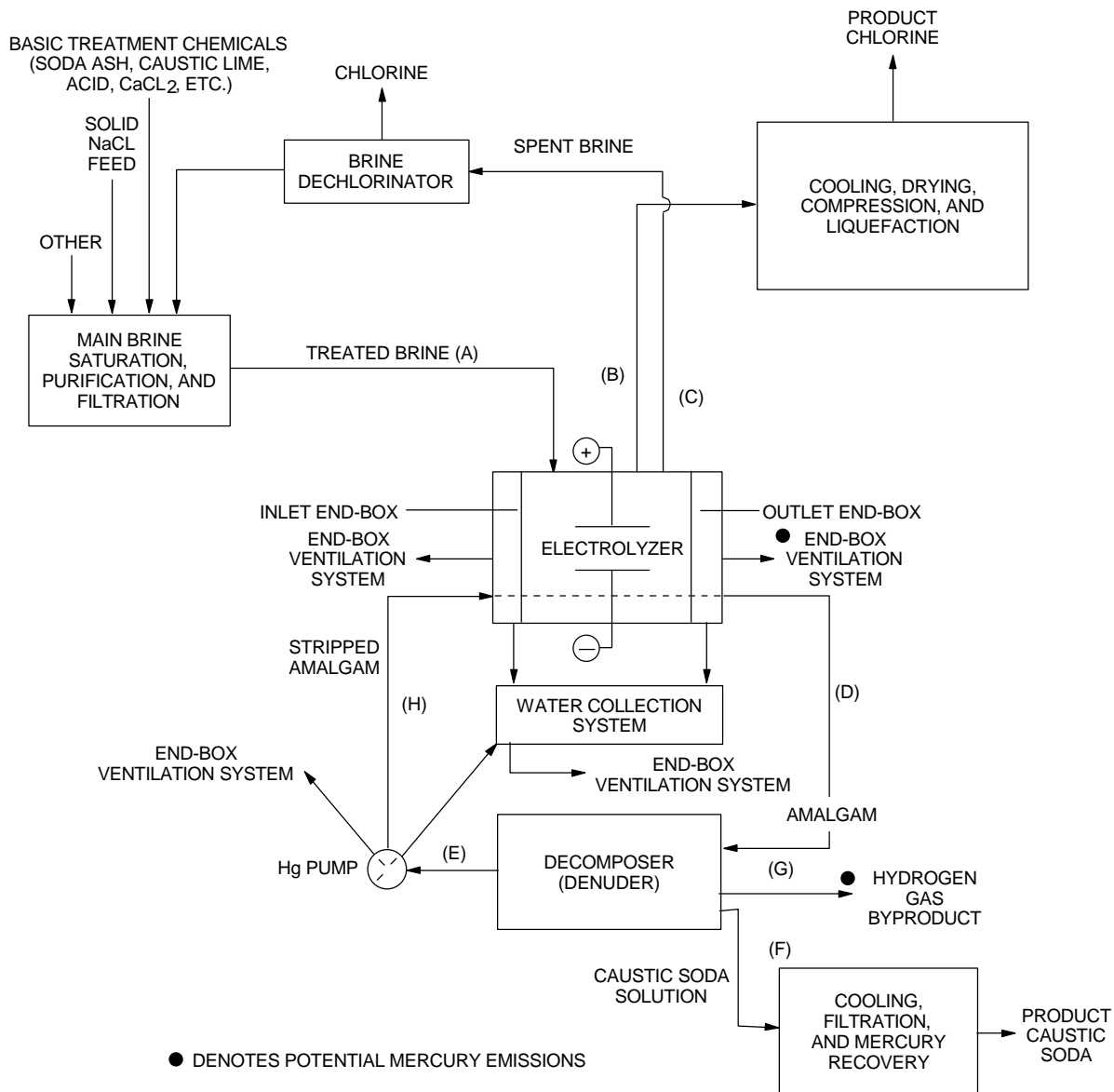


Figure 5-1. Basic flow diagram for a mercury-cell chlor-alkali operation⁹.

Chlorine gas (Stream B), formed at the electrolyzer anode, is collected for further treatment. The spent brine (Stream C) contains 21-22 weight percent NaCl and is recycled from the electrolyzer to the main brine saturation section through a dechlorination stage. Sodium forms an amalgam, containing from 0.25 to 0.5 percent sodium, at the electrolyzer cathode. The resulting amalgam flows into the outlet end box at the end of the electrolyzer. In the outlet end box, the amalgam is constantly covered with an aqueous layer to reduce mercury emissions. The outlet end box also allows removal of a thick mercury "butter" that is formed by impurities. The sodium amalgam (Stream D) flows from the outlet end box into the second cell, the decomposer.

The decomposer is a short-circuited electrical cell in which the sodium amalgam acts as the anode and graphite as the cathode in sodium hydroxide solution. Fresh water is added to the decomposer where it reacts with the sodium amalgam to produce elemental mercury (Stream E), sodium hydroxide (Stream F), and byproduct hydrogen gas (Stream G). Stream E is then stripped of sodium and the mercury (Stream H) is recirculated back to the electrolyzer through the inlet end box. The inlet end box provides a convenient receptacle on the inlet end of the electrolyzer to receive the recycled mercury from the decomposer and keep it covered with an aqueous layer to reduce mercury emissions.

The caustic soda solution (Stream F) leaving the decomposer at a typical concentration of 50 weight percent is cooled and filtered. The byproduct hydrogen gas (Stream G) may be vented to the atmosphere, burned as a fuel, or used as a feed material for other processes.^{9,14}

5.1.2 Emission Control Measures

Several control techniques are employed to reduce the level of mercury in the hydrogen streams and in the ventilation stream from the end boxes. The most commonly used techniques are (1) gas stream cooling, (2) mist eliminators, (3) scrubbers, and (4) adsorption on activated carbon or molecular sieves. Mercury vapor concentrations in the cell room air are not subject to specific emission control measures but rather are maintained at acceptable worker exposure levels using good housekeeping practices and equipment maintenance procedures.

Gas stream cooling may be used as the primary mercury control technique or as a preliminary removal step to be followed by a more efficient control device. The hydrogen gas stream from the decomposer exits the decomposer at 93° to 127°C (200° to 260°F) and passes into a primary cooler. In this indirect cooler, a shell-and-tube heat exchanger, ambient temperature water is used to cool the gas stream to 32° to 43°C (90° to 110°F). A knockout container following the cooler is used to collect the mercury. If additional mercury removal is desired, the gas stream may be passed through a more efficient cooler or another device. Direct or indirect coolers using chilled water or brine provide for more efficient mercury removal by decreasing the temperature of the gas stream to 3° to 13°C (37° to 55°F). If the gas stream is passed directly through a chilled water or brine solution, the mercury condenses and is collected under water or brine in lined containers. Mercury in the ventilation air from the end boxes can be removed using either direct or indirect cooling methods. In situations where the ventilation air from the exit box contains mercuric chloride particulates, the direct method may be preferred. The direct cooling method not only cools the gas stream, but also removes the particulate from the stream. Regardless of the gas stream treated, the water or brine from direct contact coolers requires water treatment prior to reuse or discharge because of the dissolved mercury in the liquid.

Mist eliminators can be used to remove mercury droplets, water droplets, or particulate from the cooled gas streams. The most common type of eliminator used is a fiber pad enclosed by screens. With the fiber pad eliminator, trapped particles are removed by periodic spray washing of the pad and collection and treatment of the spray solution.

Scrubbers are used to chemically absorb the mercury from both the hydrogen stream and the end box ventilation streams. The scrubbing solution is either depleted brine from the mercury cell or a sodium hypochlorite (NaOCl) solution. These solutions are used in either sieve plate scrubbing towers or packed-bed scrubbers. Mercury vapor and mist react with the sodium chloride or hypochlorite scrubbing solutions to form water-soluble mercury complexes. If depleted brine is used, the brine solution is transferred from the scrubber to the mercury cell where it is mixed with fresh brine and the mercury is recovered by electrolysis in the cell.

Sulfur- and iodine-impregnated carbon adsorption systems are commonly used to reduce mercury levels in the hydrogen gas and end box streams. This method requires pretreatment of the gas stream by

primary or secondary cooling followed by mist eliminators to remove about 90 percent of the mercury content of the gas stream. As the gas stream passes through the carbon adsorber, the mercury vapor is initially adsorbed by the carbon and then reacts with the sulfur or iodine to form the corresponding mercury sulfides or iodides. Depending upon the purity requirements and final use for the hydrogen gas, several adsorber beds may be connected in series to reduce the mercury levels to the very low ppb range.

A proprietary molecular sieve adsorbant was used by five facilities to remove mercury from the hydrogen gas stream until 1984 when the supply of the adsorbant was discontinued by the manufacturer. The technique used dual adsorption beds in parallel such that while one bed was being used for adsorption, the other was being regenerated. A portion of the purified hydrogen gas from one adsorption bed was diverted, heated, and used to regenerate the second adsorption bed.⁹

In addition to the control measures described above, the conversion of mercury cell chlor-alkali plants to the membrane cell process would eliminate all mercury emissions from this industry. As mentioned earlier, the chlor-alkali industry is gradually moving away from mercury cell production and toward the membrane cell process.

5.1.3 Emissions

The three primary sources of mercury emissions to the air are (1) the byproduct hydrogen stream, (2) end box ventilation air, and (3) cell room ventilation air. Emission sources (1) and (2) are indicated on Figure 5-1 by solid circles.

The byproduct hydrogen stream from the decomposer is saturated with mercury vapor and may also contain fine droplets of liquid mercury. The quantity of mercury emitted in the end box ventilation air depends on the degree of mercury saturation and the volumetric flow rate of the air. The amount of mercury in the cell room ventilation air is variable and comes from many sources, including end box sampling, removal of mercury butter from end boxes, maintenance operations, mercury spills, equipment leaks, cell failure, and other unusual circumstances.⁹

Mercury emissions data for end box ventilation systems and hydrogen gas streams from 21 chlor-alkali production facilities are included in a 1984 EPA report.⁹ The dates of the emission tests included in the report range from 1973 to 1983. These data should not be applied to current mercury cell operations in part because of the variability in the emission data reported. No evaluation of the variability in the data was presented in the EPA report. In addition, control techniques at current facilities differ from the techniques employed during these tests. Even if the general technique (e.g., scrubbing, carbon adsorption) is the same, improvements in control efficiency have likely been made since these tests were conducted.

The most recent AP-42 section on the chlor-alkali process presents emission factors for emissions of mercury from mercury cell hydrogen vents and from end boxes.²⁸ These emission factors are based on two 1972 emission test reports. The emission factors were not used to estimate emissions from the chlor-alkali industry because process operations and control techniques have likely changed considerably since these tests were conducted. If available, recent test data and information on control system design and efficiency should be used to estimate emissions for site-specific mercury cell operations.

Total 1994 mercury emissions for this industry are estimated to be 6.5 Mg (7.1 tons); see Appendix A for details.

5.2 BATTERY MANUFACTURING

Three main types of primary batteries have historically used mercury: (1) mercuric oxide (also known as mercury-zinc); (2) alkaline; and (3) zinc-carbon (or Leclanché). The mercury served two principal functions: (1) in the cathode of mercuric oxide batteries and (2) as an inhibitor for corrosion and side reactions in zinc-carbon and alkaline batteries. Zinc air, silver oxide, and alkaline manganese button cell batteries also use very small amounts of mercury to control gassing. Prior to the late 1980's, most primary batteries and some storage batteries contained mercury in the form of mercuric oxide (HgO), zinc amalgam (Zn-Hg), mercuric chloride (HgCl₂), or mercurous chloride (Hg₂Cl₂). Since 1989, the use of mercury in primary batteries has decreased from 250 Mg (275 tons) in 1989 to less than 0.5 Mg (<0.6 tons) in 1995 (see Table 3-2). The two major reasons for this decrease were reduction in the production of mercuric oxide batteries and the discontinued use of mercury as a corrosion inhibitor in alkaline and zinc carbon batteries. This decrease occurred as a result of the enactment on May 13, 1996 of the "Mercury-Containing and

Rechargeable Battery Management Act” (Public Law 104-142). Upon enactment, this law prohibited the sale of mercuric oxide button cells and alkaline batteries containing mercury as well as the use of mercury as a corrosion inhibitor in zinc carbon batteries. Under the law, it also became illegal to sell larger mercuric oxide batteries unless the manufacturer or importer provides purchasers with information on licensed recycling or disposal facilities. The sale of mercury oxide button cells was discontinued as early as 1993 and use of mercury as a corrosion inhibitor in alkaline batteries ceased in 1992-1993.²⁹ Since the only type of battery that uses mercury to any measurable degree is the mercuric oxide, it is the only battery discussed in this section.

Table 5-2 presents the U.S. manufacturers and production sites for mercuric oxide, alkaline manganese, or zinc-carbon batteries in 1996. The only facilities that produce mercuric oxide batteries are AMC, Inc. and Eveready in Bennington, Vermont.

TABLE 5-2. MERCURIC OXIDE, ALKALINE MANGANESE, OR ZINC-CARBON BATTERY MANUFACTURERS IN 1996

Manufacturer	Production site
Alexander Manufacturing Company (AMC, Inc.)	Mason City, IA
Duracell, USA	Cleveland, TN LaGrange, GA Lancaster, SC Lexington, NC
Eagle-Picher Industries, Inc.	Colorado Springs, CO
Eveready Battery Company, Inc.	Maryville, MO Fremont, OH (to be closed) Bennington, VT Asheboro, NC (2 plants)
Mutec ^a	Columbus, GA (Corporate offices)
Rayovac Corp.	Madison, WI Fennimore, WI Portage, WI

Source: References 29 and 33.

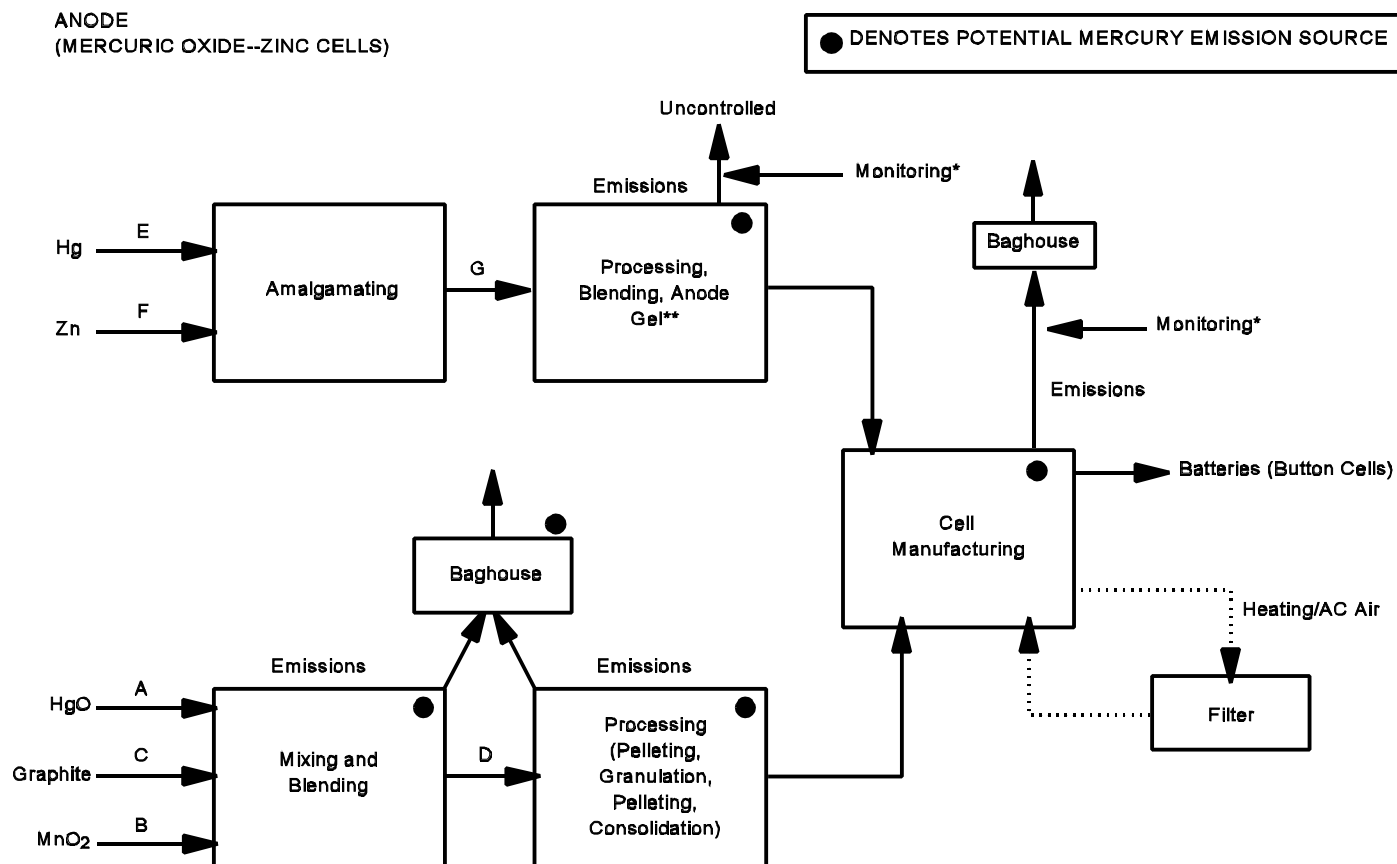
^aMutec is a joint venture between Eastman Kodak and Panasonic.

Mercuric oxide batteries were produced in two sizes: button cells and larger sizes. Button cells are small, circular, relatively flat batteries that were used in transistorized equipment, walkie-talkie's, photoelectric exposure devices, hearing aids, electronic watches, cardiac pacemakers, and other items requiring small batteries. Larger mercuric oxide batteries are produced for a variety of medical, military, industrial, and other nonhousehold equipment.

5.2.1 Process Description

The basic flow diagram for the manufacture of mercuric oxide batteries is shown in Figure 5-2. The mercuric oxide-zinc cells use mercuric oxide (mixed with graphite and manganese dioxide) as the cathode. The anode is a zinc-mercury amalgam. According to the NEMA, the basic flow diagram in Figure 5-2 was based on a Rayovac mercuric oxide battery production facility in Portage, Wisconsin, that discontinued production of this battery type in 1986.³⁰

In the production of the cathodes, mercuric oxide (Stream A), manganese dioxide (Stream B), and graphite (Stream C) are manually metered through a hopper to the blending area.⁹ The resulting mixture (Stream D) is sent to a processing unit where it is compacted into tablets by "slugging" (compression in a rotary pressing device to a specified density). These tablets are then granulated into uniformly sized



CATHODE
(MERCURIC OXIDE--ZINC & MERCURIC OXIDE--CADMIUM CELLS)

*Mercury emissions monitored to ensure compliance with state limits.

**Process operations controlled to maintain compliance with state emission limits.

Figure 5-2. General flow diagram for mercuric oxide battery (button cell) manufacture.

particles, and then pelletized in a rotary press. The pellets are consolidated into small metal cans less than 1.3 cm (0.5 in.) in diameter.⁸

For the production of the anodes, elemental mercury (Stream E) and zinc powder (Stream F) are metered from hoppers or hold tanks into an enclosed blender to produce a zinc-mercury amalgam. The amalgam (Stream G) is sent to a processing area where it is blended and the anode gel formed.⁸ Highly controlled process operations are enforced to maintain mercury vapor emissions to levels within compliance to State limits.

The completed anodes and cathodes then are sent to the cell manufacturing area. Separators, electrolyte, and other components are assembled with the anode and cathode to produce the HgO-Zn cell. Assembly may be automatic or semiautomatic. The assembled cathode, anode, electrolyte, and cover are sealed with a crimper. Depending on the design, other components may be added. Those additional components may include an insulator, an absorber, and a barrier.

An integrated mercuric oxide battery plant may also produce HgO and recycled mercury onsite. Mercuric oxide production is discussed in Section 4 under mercury compound production. Secondary recovery of mercury at the battery plant is discussed in Section 4 under secondary mercury production.

5.2.2 Emission Control Measures

Baghouses are used to control particulate emissions from the mixing/blending and processing steps in the production of cathodes. Mercury vapor emissions from the anode processing and cell manufacturing areas are generally discharged to the atmosphere uncontrolled. Ventilation air in the assembly room is recirculated through particulate filters. One plant reported an average of 73 percent mercury vapor removal efficiency in the cell assembly room when an air handler system, consisting of a particulate prefilter and a charcoal filter, was operated using 75 percent recirculating air and 25 percent fresh air.⁸

In addition to the emission control measures, other methods can be used to reduce potential worker exposure in the workplace.⁸ Table 5-3 summarizes the types of methods used in the workplace to reduce worker exposure to mercury vapor and particulate during battery manufacturing.

TABLE 5-3. METHODS FOR REDUCING WORKER EXPOSURE TO MERCURY EMISSIONS IN BATTERY MANUFACTURING

Control methods	Particulate	Vapor
Process modification and substitution	X ^a	
Containment	X ^a	X ^{d,e}
Ventilated enclosure	X ^{b,c}	X ^{d,e}
Local exhaust ventilation	X ^{a,b,c}	X ^{d,e}
Temperature control		X ^{d,e}
Dilution ventilation	X ^{a,b,c}	X ^{d,e}
Isolation	X ^{a,c}	X ^{d,e}
Mercury removal from air stream	X ^{a,b,c}	
Personal protective equipment	X ^{a,b}	

Source: Reference 8.

^aParticulate emissions during loading of mixers and blenders in cathode preparation.

^bParticulate emissions from grinding, slugging, and pelletizing in cathode production.

^cParticulate emissions from drying, screening, and pelletizing in anode production.

^dVapor emissions from blending, drying, and pelletizing during anode production.

^eVapor emission from product components.

Reject materials such as anodes, cathodes, chemical mixes, and cells can be stored under water to suppress mercury vaporization.

Machinery for grinding, mixing, screening, pelletizing, and/or consolidating can be enclosed with little or no need for worker access. Two mercuric oxide button cell manufacturers in 1983 were using such enclosures and glove boxes to reduce worker exposure. Iris ports allowed access to the enclosed equipment. Exhaust airstreams are generally ducted to a baghouse. These facilities also used ventilated enclosures to store completed anodes and cathodes on the cell assembly lines; the exhaust air takeoffs from these enclosures led to a baghouse.

5.2.3 Emissions

During the manufacture of mercuric oxide batteries, mercury may potentially be emitted from several processes as particulate and as vapor emissions. These release points are indicated in Figure 5-2 by a solid circle. The processes include grinding, mixing, sieving, pelleting, and/or consolidating.

The only reported emission factor for a mercuric oxide production facility was for one plant in Wisconsin.³¹ This facility used a combination of a baghouse and charcoal filter to treat the exhaust ventilation air. Annual use of mercury was 36.17 Mg (39.8 tons) and annual emissions were reported as 36.3 kg (80 lb) of mercury as HgO particles. For this specific facility, the mercury emission factor would be 1.0 kg/Mg (2.0 lb/ton) of mercury used. This facility discontinued production of mercuric oxide batteries in 1986.³⁰

This emission factor should be used with extreme caution for several reasons. The facility ceased production of mercuric oxide batteries and the emission controls cited in Reference 31 are probably not applicable to facilities currently producing this type of battery. Although it is not specifically stated in Reference 31, it is also presumed that the mercury emission quantity was an estimate by the manufacturer because no reference is made to any emissions testing performed at the facility. Moreover, this factor is for 1 year at one specific site so that extrapolation of this factor to current mercuric oxide battery manufacturing facilities can lead to erroneous results.

Based on another study, the emission source rates from an integrated mercury button cell plant are summarized in Table 5-4.⁹ Major emission points were the pelleting and consolidating operations (up to 42 g/d; 0.094 lb/d) and cell assembly (29 g/d; 0.063 lb/d). Emission controls were not in place for mercury vapor emissions from the main plant.

Total 1995 mercury emissions for this industry are estimated to be 5×10^{-4} Mg (6×10^{-4} tons); see Appendix A for details.

5.3 ELECTRICAL USES

Mercury is one of the best electrical conductors among the metals and is used in five areas of electrical apparatus manufacturing: electric switches, thermal sensing elements, tungsten bar sintering, copper foil production, and fluorescent light manufacture.

5.3.1 Electric Switches

The primary use of elemental mercury in electrical apparatus manufacturing is in the production of silent electric wall switches and electric switches for thermostats. The mercury "buttons" used in wall switches consist of mercury, metal electrodes (contacts), and an insulator. The thermostat switches are constructed of a short glass tube with wire contacts sealed in one end of the tube. An outside mechanical force or gravity activates the switch by causing the mercury to flow from one end of the tube to the other, thus providing a conduit for electrical flow.

The National Electrical Manufacturers Association (NEMA) was contacted in 1993 to identify manufacturers of electric switches that may use mercury in their devices.³² Of the 15 companies identified by NEMA in 1993, 10 currently use no mercury at their production facilities. General Electric Corporation stated that thermostats, both with and without mercury, were produced at their Morrison, Illinois, facility. Honeywell, Inc. produces microswitches that contain mercury at their Freeport, Illinois, facility. The only use of mercury by Emerson Electric is by its White Rodgers Company that manufactures mercury bulb switches at a plant in Afton, Missouri and mercury bulb switches, used for thermostats, at a plant in Puerto Rico.²⁹ No information is available for the two companies shown below.

TABLE 5-4. EMISSION SOURCE PARAMETERS FOR AN INTEGRATED
MERCURY BUTTON CELL MANUFACTURING FACILITY

Building/source No. description ^a	Emission rate ^b		Exit temp., °K, and control device
	g/d	lb/d	
Main Plant			
Control Room			
1. Blending, slugging, compacting, granulating	6.12	0.0135	297; Baghouse
2. Slugging, granulating	1.22	0.0027	297; Baghouse
3. Pelleting, consolidating	1.63 ^c	0.0036 ^c	295; Baghouse
4. Pelleting, consolidating	42.46	0.0936	297; Baghouse
4a. Pelleting, consolidating	6.53	0.0144	297; Baghouse
5. Blending, compacting, granulating, pelleting, consolidating	1.36 ^c	0.003 ^c	297; Baghouse
Anode room			
6. Amalgam, dewatering	1.82 ^c	0.004 ^c	297; Uncontrolled
6a. Vacuum dryer	0.46 ^c	0.001 ^c	297; Uncontrolled
6b. Blending	0.91 ^c	0.002 ^c	297; Uncontrolled
7. Pelleting, zinc amalgam	4.08 ^c	0.009 ^c	295; Baghouse
Cell assembly area			
8. Assembling cells	28.58	0.0630	295; Baghouse for particulate. Vapor by recirculating air through prefilters and charcoal filters

Source: Reference 9.

^aSource numbers are the same code used by facility.

^bEmission rates were measured by facility except where noted.

^cEstimated emission rate by facility.

Company

Ranco, Inc.
United Technologies

Corporate Headquarters

Plain City, OH
Huntington, IN

In 1995, 84 Mg (92 tons) of mercury were used in the production of wiring devices and switches.²

5.3.1.1 Process Description.

5.3.1.1.1 Mercury buttons for wall switches. A process flow diagram for the manufacture of mercury buttons for wall switches is shown in Figure 5-3. A metal ring, glass preform, ceramic center, and center contact are assembled on a semiautomatic loader (Step 1) and fused together in a sealing furnace (Step 2). Each subassembly is then transferred to a rotating multistation welding machine, located in an isolation room, where it is filled with about 3 g (0.11 ounces) of mercury (Step 3). The mercury used to fill the subassembly is stored in an external container. During the subassembly filling step, the mercury container is pressurized with helium; this pressurization transfers the mercury from the large storage container to a smaller holding tank. Mercury is released in a controlled manner from the holding tank by using a rotating slide gate that is synchronized to the welding machine speed. The filled subassembly is placed in the can, evacuated, and welded shut to form the button (Step 4). The assembled buttons then leave the isolation room and are cleaned (Step 5), zinc plated (Step 6), and assembled with other components (Step 7) to form the completed wall switches.⁸

5.3.1.1.2 Thermostat switches. The production process for thermostat switches used for household heating/air conditioning control and other applications is shown in Figure 5-4. First, metal electrodes (contacts) are inserted into one end of a glass tube 0.89 to 1.5 cm (0.35 to 0.59 in.) in diameter (Step 1). This end of the tube is then heated, crimped around the electrodes, and sealed. The apparatus is then cleaned, transferred to the isolation fill room, and loaded onto the filling machine where the tubes are evacuated (Step 2). At the filling machine (Step 3), the vacuum in the glass tube is released and mercury is drawn into the tube. The open end of the mercury-filled tube is then heated, constricted, and sealed (Step 4). Filling of switch tubes produced in low volume is performed manually using the same sequence of steps. Excess glass at the seal is discarded into a bucket of water (Step 5). The filled tube leaves the isolation room and falls into a transport container (Step 6). Attachment of wire leads to the electrode contacts completes the switch assembly (Step 7).

5.3.1.2 Emission Control Measures. Table 5-5 shows typical emission control methods used in the mercury switch industry to reduce worker exposure to mercury vapor. The use of isolation rooms and automated systems for fill operations in the manufacture of mercury buttons has considerably reduced the manual handling of elemental mercury. For example, a refiner can supply mercury in 363 kg (800 lb) stainless steel storage containers that are individually mounted in steel frames to permit lifting and transport by forklift. This eliminates the need to manually transfer the mercury from 35-kg (76-lb) iron flasks to the holding tank.

The use of effective gaskets and seals allows containment of mercury in the process streams. Reject and broken switches are discarded under water to suppress mercury vaporization.

Exhaust ventilation, which is custom designed to fit specific equipment, is often used to reduce worker exposure to mercury vapor, mercury particulate, or both. For example, a specially designed circular slot hood may be used to cover the filling and welding machine. Plastic strip curtains may be suspended from the hood to help prevent airflow from the hood into the work room.

Temperature control is widely practiced as one of the most effective measures to reduce mercury emissions. Reducing the fill room temperature to between 18° and 20°C (64° and 68°F) can be effective in lowering mercury emissions. Some industry operations shut down and require personnel evacuation from the room when temperatures rise above 21°C (70°F).

Dilution ventilation of fill room air, without apparent control, has been practiced at mercury switch plants. The negative pressure in the fill room prevents escape of mercury vapor into adjacent assembly areas.

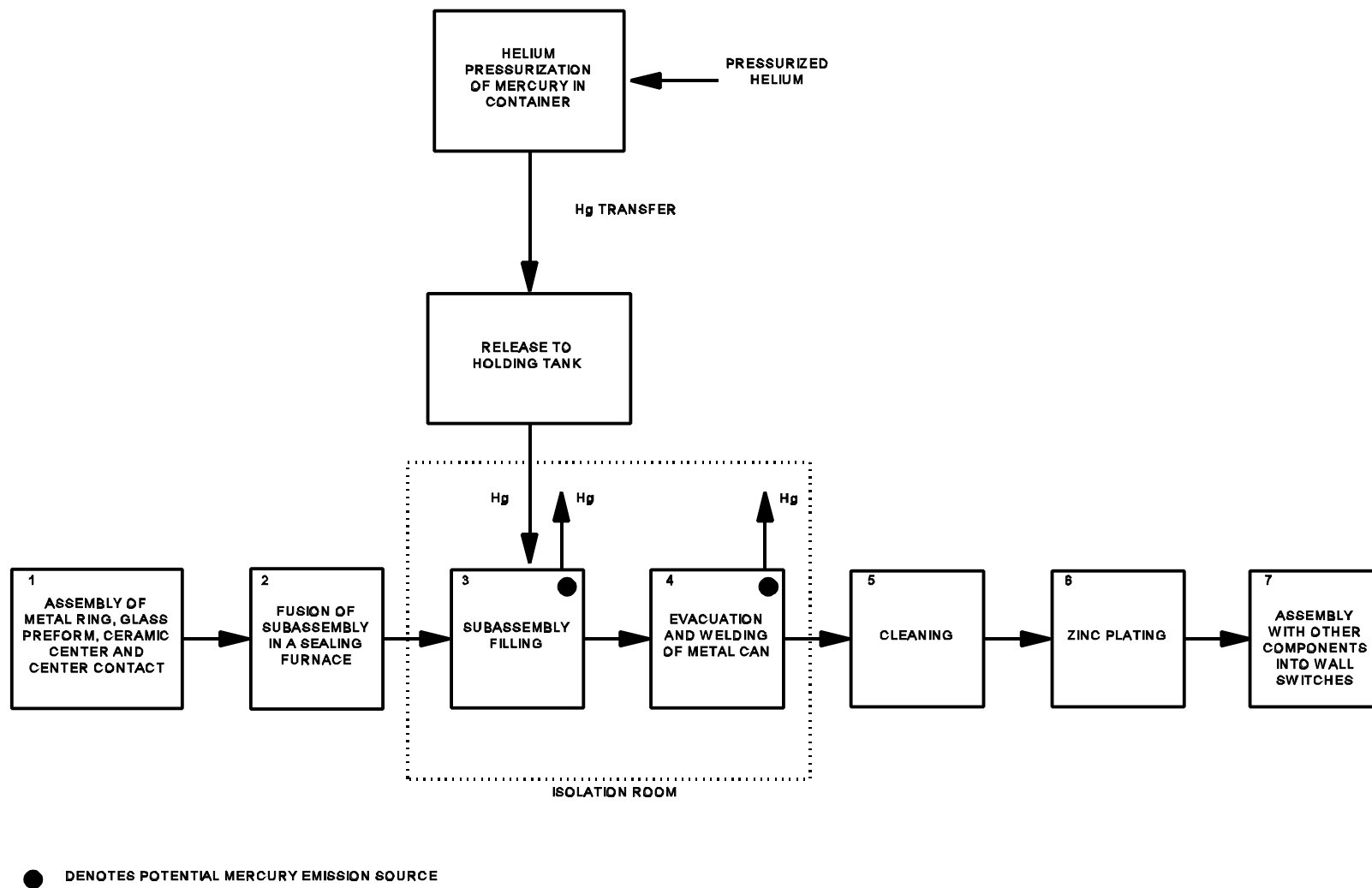


Figure 5-3. Manufacture of mercury buttons for wall switches.⁸

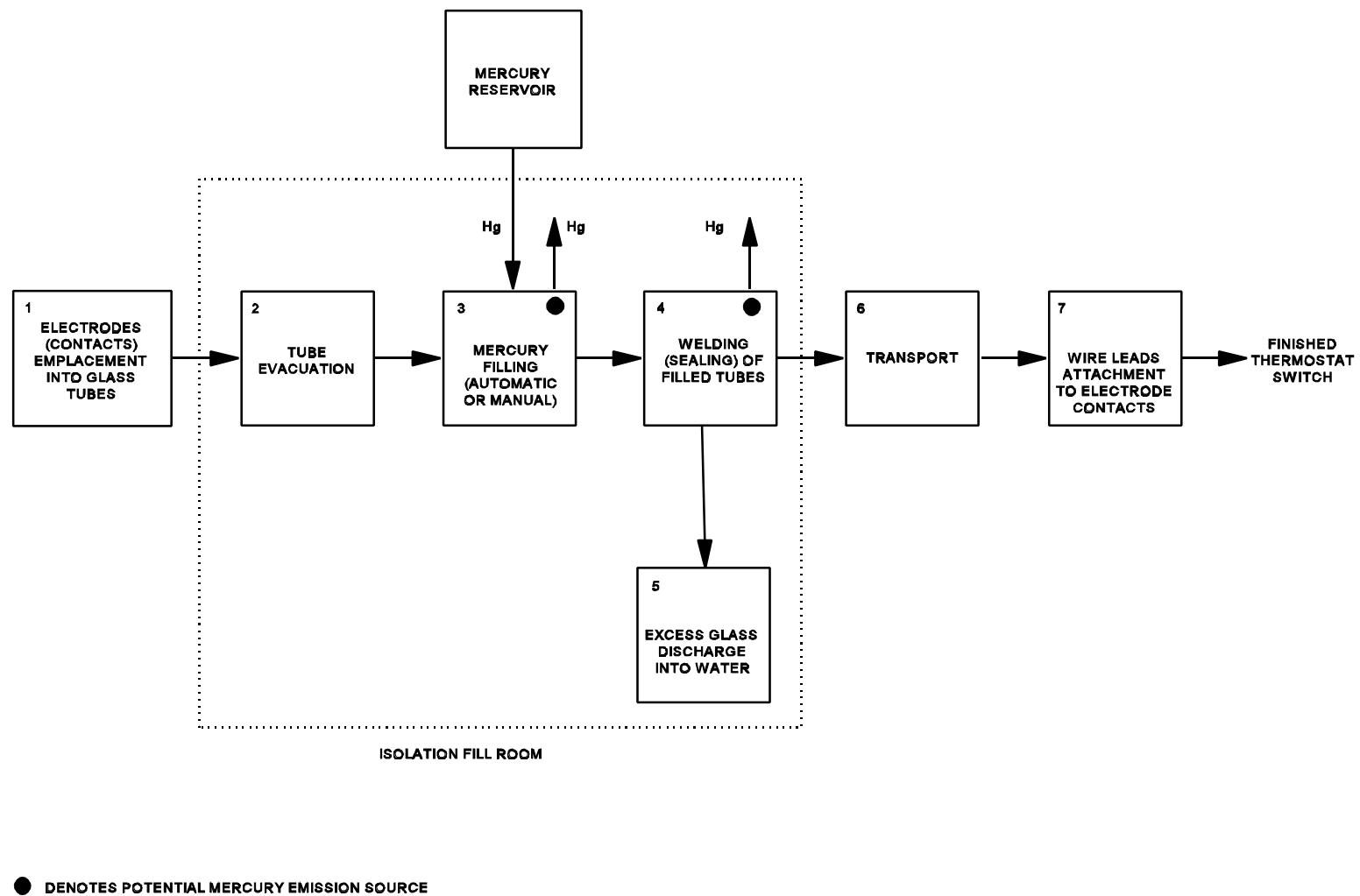
Figure 5-4. Thermostat switch manufacture.⁸

TABLE 5-5. MEASURES TO REDUCE WORKPLACE EXPOSURE TO MERCURY VAPOR EMISSIONS IN THE ELECTRIC SWITCH INDUSTRY

Control method	Sources			
	Hg purification and transfer	Hg filling	Product testing	Spills, breakage, rejects
Process modification and substitution	X			
Containment	X			X
Ventilated enclosure			X	
Local exhaust ventilation	X	X	X	X
Temperature control	X	X	X	X
Dilution ventilation	X	X	X	X
Isolation	X			

Source: Reference 8.

Examples of technologies for removing mercury from exhaust streams were not found. However, controls used at other manufacturers of electrical and electronic items may be effective at mercury switch plants. These controls are discussed in subsequent subsections.⁸

In 1994, a major manufacturer of thermostats announced a pilot project to recycle mercury thermostats. Homeowners and contractors can send unneeded thermostats back to the manufacturer so the mercury can be removed and recycled. In addition, in 1995, the U.S. EPA announced a "Universal Waste Rule" (which includes thermostats) that effectively allows for the transportation of small quantities of mercury from specific products. This ruling should encourage recycling.³³ In late 1996, the three major thermostat manufacturers, Honeywell, White Rodgers (a subsidiary of Emerson Electric), and General Electric, agreed to form the Thermostat Recycling Corporation (TRC) to initiate a nationwide mercury switch wholesaler take-back program utilizing the universal waste rule. The TRC plans to commence operations in most of the Great Lake states and Florida in late 1997 or 1998. The TRC will request participation by all contractors and wholesalers in the target states. Under the plan, HVAC dealers bring used thermostats to participating wholesalers and place the mercury-containing switch in recycling containers. When the container is full, the wholesaler ships the container to a consolidation facility where the mercury bulbs are removed from the thermostat. The mercury bulbs will be shipped to a mercury recycling facility for mercury reclamation.²⁹

5.3.1.3 Emissions. During the manufacture of electric switches (wall and thermostat), mercury may be emitted during welding or filling, as a result of spills or breakage, during product testing, and as a result of material transfer. The mercury emission sources are indicated in Figures 5-3 and 5-4 by a solid circle.

Table 5-6 lists the three manufacturers of electric switches that reported mercury air emissions in the 1994 Toxic Release Inventory (TRI). Total reported emissions from these manufacturers was 6.4 kg (14 pounds).³

TABLE 5-6. MANUFACTURERS OF ELECTRIC SWITCHES AND ELECTRONIC COMPONENTS REPORTING IN THE 1994 TOXIC RELEASE INVENTORY

Facility	Location	Comments	Total annual air emissions, lb
Durakool, Inc.	Elkhart, IN	Hg used as an article component	5
Hermaseal Co.	Elkhart, IN	Hg used as an article component	5
Micro Switch Honeywell Div.	Freeport, IL	Hg used as an article component	4

Source: Reference 3.

No mercury emission data have been published for other manufacturers of electrical switches. In the production of either mercury buttons for wall switches or thermostat switches, the principal sources of mercury emissions occur during filling processes that are conducted in isolated rooms. The isolation rooms are vented to maintain the room at a slight negative pressure and prevent mercury contamination of adjacent work areas. No emission data or results of tests are available to develop an estimate of mercury emissions from the two processes. One 1973 EPA report, however, presents an emission factor for overall electrical apparatus manufacture of 4 kg of mercury emitted for each megagram of mercury used (8 lb/ton).⁶ This factor pertains only to emissions generated at the point of manufacture. This emission factor should be used with caution, however, as it was based on engineering judgment and not on actual test data. In addition, electrical switch production and the mercury control methods used in the industry have likely changed considerably since 1973. The emission factor could, therefore, substantially overestimate mercury emissions from this industry and should not be used to estimate current mercury emissions.

Total 1995 mercury emissions for this industry are estimated to be 0.4 Mg (0.5 tons); see Appendix A for details.

5.3.2 Thermal Sensing Elements

In certain temperature-sensing instruments, a bulb and capillary temperature-sensing device is an integral part of the instrument. These devices use the expansion force of mercury as it is heated to activate the external controls and indicators of the instrument.

5.3.2.1 Process Description. A thermal sensing instrument consists of a temperature-sensing bulb, a capillary tube, a mercury reservoir, and a spring-loaded piston. The bulb is made by cutting metal tubing to the correct size, welding a plug to one end of the tube, and attaching a coupling piece to the other end. The capillary tube is cut to a specified length and welded to the coupling at the open end of the bulb. The other end of the capillary is welded to a "head" that houses the mechanical section of the sensor.

The bulb and capillary assembly are filled with mercury by a multistation mercury filling machine that is housed in a ventilated enclosure. After filling, the sensor is transferred to a final assembly station where a return spring and plunger are set into a temporary housing on the head of the sensor. To complete the temperature instrument, the sensor is then attached to a controller and/or indicating device.⁸

5.3.2.2. Emission Control Measures. No information was found on specific emission control devices or measures to control mercury emissions during the filling process. Although the filling machine is typically in a ventilated enclosure, no information is available concerning any subsequent treatment of the exhaust gas prior to discharge to the atmosphere.

5.3.2.2.1 Emissions. No emission factors for mercury emissions from thermal sensing element manufacturing were found in the literature, and no emission test data were available to calculate emission factors.

5.3.3 Tungsten Bar Sintering

5.3.3.1 Process Description. Tungsten is used as a raw material in the manufacture of incandescent lamp filaments. The manufacturing process starts with tungsten powder pressed into long, thin bars of a specified weight. These bars are pretreated and then sintered using a high-amperage electrical current. During the tungsten bar sintering process, mercury is used as a continuous electrical contact. The mercury contact is contained in pools (mercury cups) located inside the sintering unit.

After the sintering process is completed, the bars are cooled to ambient temperature and the density of the tungsten bars is determined. Metallic mercury is normally used in these measurements because of its high specific gravity. To calculate the density of the tungsten bars, the bars are dipped into a pool of mercury, and the weight of the displaced mercury is determined. When the bars are removed from the mercury pool, the mercury is brushed off into a tray of water that is placed in front of the pool.⁸

5.3.3.2 Emission Control Measures. No specific information on emission control measures for sintering tungsten bars was found in the literature.

5.3.3.3 Emissions. Mercury is used only during the actual sintering and the final density measurements. For this reason, it is assumed that these two operations account for all the mercury emitted

from the process. No specific data for mercury emissions from the tungsten sintering process were found in the literature, and no emission test data were available to calculate mercury emission factors.

5.3.4 Copper Foil Production

High purity copper foil, used as a laminate in printed circuit boards, is produced by an electrodeposition process using mercury as the electrical contact.

5.3.4.1 Process Description. The initial step in the foil production process is the dissolution of scrap copper in sulfuric acid to form copper sulfate. The solution is then fed to the plating operation where the copper ions are electrodeposited on rotating drums as copper metal. Each plating drum is composed of a concrete cell containing the copper sulfate solution, an anode (lead), a rotating titanium drum (cathode), and a winding roll. During the electrodeposition process, a current passes between the lead anode and the rotating drum cathode. As the drum rotates, the copper metal is electrodeposited on the drum surface in the form of a continuous thin foil sheet.

The plated foil is peeled from the drum and wound on a roll. When the roll reaches a specified size, it is removed from the plating drum unit and transferred to the treating room where it is specially treated, annealed, slit, wrapped, and prepared for shipping.⁸

Elemental mercury is used as the continuous electrical contact between the rotating shaft of the drum and the electrical connections. The liquid mercury is contained in a well located at one end of the rotating drum shaft.⁸

5.3.4.2 Emission Control Measures. Manufacturing processes that require mercury as an electrical contact generally use ventilated enclosures for controlling vapor emissions from mercury pools. In copper foil production, the mercury wells are located in ventilated enclosures, and exhaust gases are directed to a mercury vapor filter. Another method of controlling emissions from mercury wells is to reduce the temperature of mercury in the well. Generally, mercury wells operate at 82°C (180°F); at this temperature, mercury has a vapor pressure of 0.10 mmHg. A temperature reduction to 21°C (70°F) decreases the mercury vapor pressure to 0.0013 mmHg.

5.3.4.3 Emissions. Mercury can be emitted from the drum room and treating room of the copper plating process. No information was available on mercury release rates to the atmosphere through ventilation systems. No specific data for mercury emissions from the production of copper foil were found in the literature, and no emission test data were available for calculating emission factors.

5.3.5 Fluorescent Lamp Manufacture and Recycling

All fluorescent lamps contain elemental mercury as mercury vapor inside the glass tube. Mercury has a unique combination of properties that make it the most efficient material for use in fluorescent lamps. Of the 680 million mercury-containing lamps sold in the U.S. annually, approximately 96 percent are fluorescent lamps.³⁴ The names and division headquarters of the four fluorescent lamp manufacturers in the U.S. in 1995 are shown in Table 5-7.

TABLE 5-7. U.S. FLUORESCENT LAMP MANUFACTURERS' HEADQUARTERS

Company	Division Headquarters
DURO-LITE Corp. General Electric OSRAM Sylvania, Inc. Philips Lighting Company	North Bergen, NJ Cleveland, OH Danvers, MA Somerset, NJ

Source: References 29 and 33..

In 1995, 30 Mg (33 tons) of mercury were purchased for the manufacture of electric lighting, including fluorescent, mercury vapor, metal halide, and high-pressure sodium lamps.² Lamps do not contain all of the mercury purchased for the manufacture; mercury not retained in the lamps is returned to mercury recyclers for purification and reuse. In 1994, 15.7 Mg (17.3 tons) of the 27 Mg (30 tons) of mercury were actually contained in the lamps.³⁴

There are presently few mercury recycling facilities in the country. Data from a 1994 EPA report indicate that approximately 600 million fluorescent lamps are disposed each year, with only 2 percent of that number being recycled.³⁵ That translates into approximately 12 million fluorescent lamps recycled annually. The number of fluorescent lamps recycled has been increasing so the 2 percent figure in the 1994 report may underestimate the current recycling efforts.

5.3.5.1 Fluorescent Lamp Manufacture.

5.3.5.1.1 Process description. Fluorescent lamp production begins with the preparation of the lamp tube. Precut glass tubes are washed to remove impurities, dried with hot air, and coated with a liquid phosphor emulsion that deposits a film on the inside of the lamp tube. Mount assemblies, consisting of a short length of glass exhaust tube, lead wires, and a cathode wire, are fused to each end of the glass lamp tube. The glass lamp tube, with attached mount assemblies, is then transferred to the exhaust machine.

On the exhaust machine, the entire glass tube system is exhausted and a small amount (15 to 100 mg [3.3×10^{-5} to 2.2×10^{-4} lb]) of mercury is added. A few high wattage HID lamps may contain up to 250 mg of mercury. Over the life of the lamp, some of the mercury combines with the glass, internal metals, and the emulsion coating on the interior of the lamp tube. Following the addition of mercury, a vacuum is drawn through the glass lamp tube system to remove the air and small quantities of excess mercury. The glass tube system is then filled with inert gas and sealed. After the lamp tubes are sealed, metal bases are attached to the ends of the lamp tube and are cemented in place by heating.⁸

5.3.5.1.2 Emission control measures. No add-on emission control measures were identified for exhaust or ventilation gases. The only methods identified were those used to reduce worker exposure. Mercury air concentrations due to handling are usually reduced by containment, local exhaust ventilation, temperature control, isolation, and/or mercury removal from the air stream. Mercury air levels during the lamp production steps are reduced by process modifications, containment, ventilated enclosures, local exhaust ventilation, and temperature control.

The use of mercury-containing fluorescent and other high-efficiency lighting systems is increasing because of the energy efficiency of these systems. However, the mercury content of fluorescent lamps has decreased by 53 percent between 1989 and 1995 to an average of 22.8 mg of mercury per lamp. Continued product design changes that further reduce mercury use by the industry could also further reduce mercury emissions from the industry.

5.3.5.1.3 Emissions. Mercury emissions from fluorescent lamp manufacturing may occur during mercury handling operations and during lamp production. Handling operations that may result in mercury vapor emissions include mercury purification, mercury transfer, and parts repair. During lamp production, mercury may be emitted from the mercury injection operation and from broken lamps, spills, and waste material.

One 1973 EPA report presents an emission factor for overall electrical apparatus manufacture of 4 kg of mercury emitted for each megagram of mercury used (8 lb/ton).⁶ This factor pertains only to emissions generated at the point of manufacture. This emission factor should be used with extreme caution, however, as it was based on engineering judgment and not on actual test data. In addition, electric light production and the mercury control methods used in the industry have likely changed considerably since 1973. The emission factor may, therefore, substantially overestimate mercury emissions from this industry.

A 1984 emission rate of 10.2 g/d (0.02 lb/d) was found in the National Air Toxics Information Clearinghouse (NATICH) for a GTE lamp manufacturing facility in Kentucky.³⁶ However, no information was available on the quantity of mercury used at the facility, the number of units produced, or other data that would permit a comparison of this emission rate with other facilities. In addition, no data were presented to allow calculation of an annual quantity.

Only one lamp manufacturing facility (General Electric Company Bucyrus Lamp Plant) reported mercury emissions in the 1994 TRI; their annual emissions were 0.21 Mg/yr (0.23 tons/yr).³

5.3.5.2 Fluorescent Lamp Recycling.

5.3.5.2.1 Process description. The crushing of fluorescent lamps to separate the glass from the phosphor powder in the lamp is commonly the first step in recycling of mercury; although some companies use other methods, such as removal of the phosphor powder by air vortex or by flushing with hydrochloric acid.³⁵ The simplest crushers are essentially single units with a crusher mounted on top of a barrel, usually a 55-gallon drum. This system is used in many industrial facilities to crush their fluorescent lamps as a means to reduce the solid waste volume before disposing the material in a landfill. In this version, lamps are hand-fed to a feeder chute of variable length and diameter. The lamps pass to the crushing unit, typically consisting of motor-driven blades, which implode and crush the lamps. From here, the crushed powder drops into the barrel below the crusher. Some systems include a vacuum system which collects air from beneath the crusher, preventing mercury laden air from exiting through the feed chute. Material collected in the vacuum system first passes through a cyclone separator. This removes glass particles, which drop into the drum. Air from the cyclone separator contains phosphor powder and some mercury vapor. These are removed by further control.

After crushing of the lamps, mercury recovery is often the next step in the recycling process. Most commonly, lamps that are not landfilled undergo retorting or roasting which recovers mercury by distillation. Different versions exist, but in each, the material is heated to vaporize the mercury and recover it as a liquid. This can be accomplished in closed vessels (retorts) or in open-hearth furnaces, ovens, or rotary kilns (roasting). Recovery of the vaporized mercury can be done with condensers and separators or with a venturi scrubber and decanter, followed by an air pollution control system.

Retorting generally gives higher recovery rates than does roasting, and is also well-suited to wastes containing volatile forms of mercury. Thus retorting is generally the recovery method of choice for fluorescent lamps. Typically, the mercury-containing wastes are placed in a retort, and heated for 4 to 20 hours to a temperature above the boiling point of mercury (357°C [675°F]) but below 550°C (1022°F). Vaporized material from this process is condensed in the scrubber or condenser, and then recovered in a collector or decanter. This recovered mercury may require additional treatment, such as nitric acid bubbling, to remove impurities.

5.3.5.2.2 Emission control measures. The simplest fluorescent lamp crushers have no air pollution control devices. More sophisticated versions of the barrel-mounted crusher utilize a negative air exhaust system to draw the crushed debris and prevent it from reemerging through the feeder tube. The drawn air is then passed through a high efficiency particulate air (HEPA) filter to remove particulate matter from the exhausted flow. Other control techniques include gasketing around the connection between the crusher and drum, total enclosure, and disposable collection barrels.

One crushing system utilizes a vacuum system which collects air and tube materials from beneath the crusher, which then passes through a cyclone separator to remove glass particles. From the cyclone, the air passes through a baghouse, several particulate matter filters and HEPA filters to ensure that all lamp particles have been removed. The exhaust then passes through activated carbon beds, which trap the mercury vapor. The air is then passed through more particulate filters which trap any carbon that may have been carried away from the activated carbon bed. The air from the containment room (in which the crusher and filters are located) is blended with the cleaned crusher exhaust air and sent through another series of particulate filters and more activated carbon.³⁵ No efficiencies of this control system are available.

Another crusher uses a system similar to the one mentioned above. The entire system operates under negative pressure and the crushed debris is collected in a cyclone. The exhaust continues through a reverse jet baghouse, a HEPA filter, and then through a potassium iodide-impregnated carbon filter. This removes the mercury by precipitating it in the form of mercuric iodide (no removal efficiencies were provided). The air in the building that houses the crusher is also under negative pressure and is drawn through the entire filter system as well.³⁵

No information was found describing control devices for mercury recovery systems beyond the condensers, separators, and venturi scrubbers designed for product recovery.

5.3.5.1.1 Emissions. Mercury emissions from fluorescent lamp recycling may occur from crusher feed chutes, connections between crushers and receiving barrels, collection barrels themselves, control system outlets for crushers or retorts, and scrubber system wastewater.

In many cases, actual emission estimates have not been determined for lamp recycling processes; rather, occupational exposure estimates have been derived from ambient air measurements taken in the workplace. Approximations of mercury emissions are available for two fluorescent lamp crushers based on reported production rates, air flow rates, and typical exhaust characteristics for a carbon adsorber controlling mercury vapor emissions.³⁵ The emission rates for these two crushers range from 0.14 to 10 mg/min (3.1×10^{-7} to 2.2×10^{-5} lb/min) and 0.002 to 0.16 mg/lamp (4.4×10^{-9} to 3.5×10^{-7} lb/lamp). The average emission factor for the two crushers is 0.071 mg/lamp (1.6×10^{-7} lb/lamp). This emission factor should be used with caution, however, as it was based on engineering judgment and not on actual test data.

Mercury emission test data from a 1994 test are available for one fluorescent bulb crusher. The unit is an enclosed system vented to a HEPA fabric filter and a carbon adsorber. The average mercury emission rate for the three test runs was 0.003 g/hr (0.000007 lb/hr). Using the reported tube processing rate of 3,414 bulbs/hr, a mercury emission factor of 0.00088 mg/lamp (1.9×10^{-9} lb/lamp) can be estimated which is about two orders of magnitude lower than the average emission factor estimated in the previous paragraph.³⁷

No mercury emission data were available from which to calculate emission factors for recovery processes.

5.4 INSTRUMENT MANUFACTURING AND USE (THERMOMETERS)

Mercury is used in many medical and industrial instruments for measurement and control functions including thermometers; manometers, barometers, and other pressure-sensing devices; gauges; valves; seals; and navigational devices. Because mercury has a uniform volume expansion over its entire liquid range and a high surface tension, it is extremely useful in the manufacture of a wide range of instruments. It is beyond the scope of this report to discuss all instruments that use mercury in some measuring or controlling function. Although there is potential for mercury emissions from all instruments containing mercury, this section focuses only on the production of thermometers because they represent the most significant use, and more information is available on thermometer manufacture than on the manufacture of other instruments.

There are generally two types of clinical thermometers: 95 percent are oral/rectal/baby thermometers, and 5 percent are basal (ambient air) temperature thermometers. An oral/rectal/baby thermometer contains approximately 0.61 g (0.022 oz.) of mercury and a basal thermometer contains approximately 2.25 g (0.079 oz.) of mercury.³⁸

In 1995, 43 Mg (47 tons) of mercury were used in all measuring and control instrument manufacture.²

5.4.1 Process Description

The manufacture of temperature measurement instruments varies according to the type of bulb or probe. In addition, the mercury filling procedure varies among different instrument manufacturers. The production of glass thermometers begins with the cutting of glass tubes (with the appropriate bore size) into required lengths. Next, either a glass or metal bulb, used to contain the mercury, is attached to one end of the tube.

The tubes are filled with mercury in an isolated room. A typical mercury filling process is conducted inside a bell jar. Each batch of tubes is set with open ends down into a pan and the pan set under the bell jar, which is lowered and sealed. The tubes are heated to approximately 200°C (390°F), and a vacuum is drawn inside the bell jar. Mercury is allowed to flow into the pan from either an enclosed mercury addition system or a manually filled reservoir. When the vacuum in the jar is released, the resultant air pressure forces the mercury into the bulbs and capillaries. After filling, the pan of tubes is manually removed from the bell jar. Excess mercury in the bottom of the pan is purified and transferred back to the mercury addition system or filling reservoir.

Excess mercury in the tube stems is forced out the open ends by heating the bulb ends of the tubes in a hot water or oil bath. The mercury column is shortened to a specific height by flame-heating the open ends (burning-off process). The tubes are cut to a finished length just above the mercury column, and the ends of the tubes are sealed. All of these operations are performed manually at various work stations. A temperature scale is etched onto the tube, completing the assembly.^{8,9}

5.4.2 Emission Control Measures

Vapor emissions from mercury purification and transfer are typically controlled by containment procedures, local exhaust ventilation, temperature reduction to reduce the vapor pressure, dilution ventilation, or isolation of the operation from other work areas. The tube bore size also can be modified to reduce the use of mercury.

The major source of mercury emissions in the production of thermometers may be in the mercury filling step. Several emission control measures have been identified for production processes that require, in part, filling an apparatus with metallic mercury. In the previous discussion of the electric switch industry, Table 5-5 presented several control methods that are used by that industry to reduce workplace exposure to mercury vapor emissions. These controls or combinations of controls are generally applicable to the production of thermometers.

One of the latter steps in the production of thermometers involves heating the mercury in a high temperature bath and the subsequent heating of the open ends with a flame (burning-off process). A possible control scenario for these operations would include an isolation room with local exhaust ventilation and dilution ventilation, to create a slight negative pressure in the room. This arrangement would prevent escape of mercury vapor into adjacent assembly or work areas.

Additionally, product substitutions in the marketplace may reduce mercury emissions from instrument manufacturing and use. One notable example of such a substitution is the replacement of mercury thermometers with digital devices.

5.4.3 Emissions

Mercury emissions can occur from several sources during the production of thermometers. Many of the procedures used in thermometer production are performed manually, and as a result, emissions from these procedures are more difficult to control. The most significant potential sources of emissions are mercury purification and transfer, mercury filling, and the heating out (burning-off) process. Vapor emissions due to mercury spills, broken thermometers, and other accidents may contribute to the level of mercury emissions.

No specific data for mercury emissions from manufacturing thermometers or any other instrument containing mercury were found in the literature, and no emission test data were available from which to calculate emission factors. One 1973 EPA report, however, presents an emission factor for overall instrument manufacture of 9 kg of mercury emitted for each megagram of mercury used (18 lb/ton).⁶ This emission factor should be used with extreme caution, however, as it was based on survey responses gathered in the 1960's and not on actual test data. In addition, instrument production and the mercury control methods used in instrument production have likely changed considerably since the time of the surveys.

Total 1995 mercury emissions for this industry are estimated to be 0.4 Mg (0.5 tons); see Appendix A for details.